Live ^{107}Pd in the Early Solar System and Implications for Planetary Evolution

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We present a report on the status of ^{107}Pd ($\tau = 9.4 \times 10^6$ y) in the early solar system and the implications of its presence for protoplanet evolution. Over the last two decades we have carried out an extensive search for the evidence of presently extinct ^{107}Pd in meteorites. From these results we conclude that: 1) ^{107}Ag* (excess ^{107}Ag) is present in a wide variety of iron and stony-iron meteorites; 2) ^{107}Ag* is due to the *in situ* decay of ^{107}Pd in these meteorites; 3) Pd-Ag metal - FeS and metal whole-rock isochrons have been established for a few meteorites; 4) the correlation observed for the total metal isochrons reflects a large variation in normal silver contents (~10^3) with much small variations in Pd contents (factors of 10); 5) there is a wide range in apparent ^{107}Pd/^{108}Pd ratios but many samples show a narrow range (^{107}Pd/^{108}Pd = 1.5 - 2.5 x 10^{-5}); and 6) there are clear cases of complex or pathologic behavior relating to some sulfides and their associated metal phases. The ^{107}Pd-^{107}Ag chronometer reflects the times of major chemical fractionation of Pd and Ag. The scenarios we have postulated to explain the Pd/Ag fractionation include two basically different fractionation processes, namely nebular and planetary. Major fractionation between Pd/Ag can only be achieved during condensation, early accretion, and metal segregation in the solar nebula. The reaction of FeNi with H_2S gas to form FeS and subsequent melting and segregation of FeNi and FeS provides a mechanism for minor (x2) fractionation. For some volatile-depleted meteorites, the processes of condensation of FeNi with isolation from later condensates effectively fractionated Pd/Ag and produced metal with a ^{108}Pd/^{109}Ag ~10^4 - 10^5. For other meteorites not so extensively depleted in volatiles, a smaller degree of effective Pd/Ag fractionation is produced due to the presence of later condensates which, upon planetary melting, produced metal with a ^{108}Pd/^{109}Ag ~ 50-100. Some fractionation of Pd and Ag occurred by metal-liquid, metal-crystal fractionation during crystallization in planets similar to the models of *Scott* [1972], *Larimer and Anders* [1967], and *Wai and Wasson* [1977]. If the variation in initial ^{107}Pd/^{108}Pd among meteorites indicates a time difference (ΔT) in the condensation and melting-segregation of planetesimals, the data indicate a total range of ~12 my for many meteorites. This tight cluster includes samples of the IIAB, IIIAB, IVA, IVB, and "anomalous" groups, as well as mesosiderites and pallasites. However, some meteorites exhibit no evidence of ^{107}Pd. A comparison of ^{107}Pd and ^{53}Mn ($\tau = 5.3 \times 10^6$ y) chronometers on the same meteorites is possible for a few samples. In one case, ^{107}Pd/^{108}Pd and ^{53}Mn/^{55}Mn from Cape York (group IIIA) show values of ~2×10^{-5}. In other cases, group IIIAB irons show ^{107}Pd/^{108}Pd ~2×10^{-5}, but a much smaller ^{53}Mn/^{55}Mn ~1×10^{-6}. In addition, ^{107}Pd is absent in the metal of the Eagle Station pallasite, but has ^{53}Mn/^{55}Mn = 2.3×10^{-6} in the Eagle Station silicates. There appear to be major discrepancies between the ^{107}Pd and ^{53}Mn chronometers. The ^{53}Mn-^{53}Cr system may be affected by the formation or equilibration of the microscopic phases containing Mn and Cr and the FeNi "host" during extended cooling and exsolution reaction.

1. INTRODUCTION

Earth Processes: Reading the Isotopic Code
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The purpose of this report is to update our knowledge of the presence of ^{107}Pd (mean life, $\bar{\tau}_{107} = 9.4 \times 10^6$y) in the

early solar system and the implications for iron meteorite evolution. *Kelly and Wasserburg* [1978] discovered excess ^{107}Ag from ^{107}Pd decay. We present a review of all existing Pd and Ag isotope data as of December 1994. These include data published previously [*Kelly and Wasserburg*, 1978; *Kaiser and Wasserburg*, 1983; *Chen and Wasserburg*, 1983, 1990a, 1995] and new data on the following: a) Iron meteorites: El Sampal (IIIA), Trenton (IIIA), Bear Creek (IIIB), Mt. Edith (IIIB), Chupaderos (IIIB), Duchesne (IVA), Social Circle (IVA), Tawallah Valley (IVB), Klondike (IVB), Tucson (AN) and N'Goureyma (AN); b) Chondrites: Rose City (H5), Floyd (L4); c) Pallasites: Eagle Station, Brenham and Glorieta Mountain; and d) Mesosiderites: Morristown, Emery and the unusual stony-iron meteorites, Horse Creek and Bencubbin. Some of these new data have been presented at Lunar and Planetary Science Conferences [*Chen and Wasserburg*, 1990b, 1991, 1995]. The presence of excess ^{107}Ag (^{107}Ag*) will be shown to be common in a wide variety of meteorites. On the basis of these observations, we can try to establish a self-consistent model for the timescale for condensation as well as for the physical and chemical conditions during formation and evolution of meteorite parent bodies.

The isotope ^{107}Pd was attributed to both the *s*- and *r*-process [*Burbidge et al.*, 1957]. It is produced along the main neutron capture chain and can be made in AGB stars [*Cameron*, 1993]. Because of this and its relatively long lifetime, ^{107}Pd has been used by *Wasserburg et al.* [1993, 1994] as a key index of AGB production and of the dilution of the protosolar ISM by the AGB envelope. The search for ^{107}Ag* has a long history starting with the proposal by Urey (personal communication, 1955) when the first effort to detect ^{129}Xe* in meteorites yielded a negative result [*Wasserburg and Hayden*, 1955]. The first effort to find ^{107}Ag* were by *Hess et al.* [1957]. In a subsequent effort, *Murthy* [1960, 1962] claimed to have discovered ^{107}Ag* in samples of iron meteorites such as Toluca and Canyon Diablo which have high Ag contents and low Pd/Ag ratios. However, later work by *Chakraburtty et al.* [1964] and *Dews and Newbury* [1966] did not confirm these results. All efforts to find ^{107}Ag* were hindered by experimental limitations on ion yield, by the presence of isobaric interferences (particularly by AsS^+) and by the fact that silver has only two isotopes. *Kelly and Wasserburg* [1978], following the suggestion of *Kelly and Larimer* [1977], discovered the presence of ^{107}Ag* in the iron meteorites Santa Clara (IVB group) and Piñon (anomalous group), which are very depleted in volatile elements and have high Pd/Ag values. This work used improved techniques developed for the study [*Kelly et al.*, 1978]. Further work by *Kaiser et al.* [1980a,b] and *Kaiser and Wasserburg* [1981, 1983] confirmed the existence of ^{107}Ag* in several other group IIIB, IVB and anomalous irons. These authors inferred the presence of ^{107}Ag* to be due to the *in situ* decay product of presently extinct ^{107}Pd.

While the presence of ^{107}Ag* has been discovered in many iron meteorites with high Pd/Ag, there were problems in simply attributing the ^{107}Ag* to *in situ* decay of ^{107}Pd. In particular, the troilite in Santa Clara was found to have a very high ^{107}Ag/^{109}Ag ratio 108% above normal and higher than the metal [*Kaiser and Wasserburg*, 1983]. These data are not compatible with a simple model of *in situ* decay and subsequent local Ag redistribution between metal and troilite during cooling. Furthermore, in a Pd-Ag diagram, the data on Santa Clara (IVB), Hoba (IVB), Piñon (AN), Tlacotepec (IVB), Warburton Range (IVB) and Deep Spring (AN) seem to lie on a correlation line passing through the origin instead of to the normal silver ratio. To explain these data, *Kaiser and Wasserburg* [1983] postulated a model that Ag in Santa Clara and possibly in other IVB meteorites is made up of almost pure ^{107}Ag produced from ^{107}Pd decay and of pure ^{109}Ag produced by nuclear reactions with only a small amount of normal Ag. On the other hand, *Kaiser and Wasserburg* [1983] also found that there is a good correlation between metal and troilite of Grant (IIIB). The troilite in Grant exhibits normal ^{107}Ag/^{109}Ag. Therefore, the data on Grant appear to represent a ^{107}Pd-^{107}Ag isochron and indicate that the cooling rate at elevated temperatures was sufficiently rapid to preserve this isotopic difference. Further work on Grant (IIIB) and Cape York (IIIA) by *Chen and Wasserburg* [1983], showed a good correlation of ^{107}Ag/^{109}Ag with Pd/Ag in co-existing metal and troilite. Therefore, the Pd-Ag data strongly support the suggestion that the presence of ^{107}Ag* is from *in situ* decay of ^{107}Pd on the parent planet.

An intensive study of Gibeon (IVA) by *Chen and Wasserburg* [1990a] showed that ^{107}Ag/^{109}Ag correlates with ^{108}Pd/^{109}Ag over a wide range for bulk samples of the metal (Fig. 1). The correlation line has a slope that corresponds to a ^{107}Ag*/^{108}Pd = (2.40±0.05) x 10^{-5} and extrapolates to an initial (^{107}Ag/^{109}Ag) = 1.11 ± 0.01. The metal data of Gibeon were considered to represent an isochron resulting from the *in situ* decay of ^{107}Pd in the meteorite parent body. However, the sulfide data on Gibeon show ^{107}Ag* uncorrelated with ^{108}Pd/^{109}Ag and a highly variable isotopic composition of Ag. *Chen and Wasserburg* [1990a] interpreted the sulfide data as due to diffusion transport of Ag and segregation into minor phases. Some of these complexities are clearly due to recrystallization after shock melting of FeS and possibly anthropogenic heat treatment [see extensive study by *Teshima et al.*, 1986].

In the metal phases of several other IVA group iron meteorites (Hill City, Mart, Bishop Canyon, Yanhuitlan and Ningbo) *Chen and Wasserburg* [1990a] also found the presence of ^{107}Ag* correlated with high ^{108}Pd/^{109}Ag. In a Pd-Ag diagram, data on metal from group IVA irons plot close to the Gibeon isochron and suggest that they might have a common origin. In contrast, a new analysis on Santa Clara (IVB) by *Chen and Wasserburg* [1990a] confirmed the observation that IVA and IVB are two distinct groups and

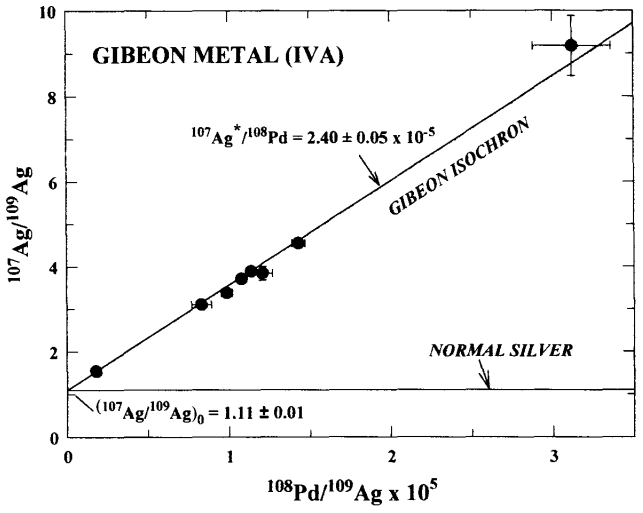

Fig. 1. Pd -Ag evolution diagram, showing all the analyzed metal samples from several different fragments of Gibeon [after *Chen and Wasserburg*, 1990a]. It can be seen that all of these data define a rather precise linear array that we interpret as an internal "total rock" isochron for Gibeon with $^{107}Pd/^{108}Pd = 2.40 \pm 0.05 \times 10^{-5}$. This will be used as a reference isochron. Note the scale compared to $(^{108}Pd/^{109}Ag)_\odot \approx 1.57$.

show very different Pd-Ag systematics. The main objectives of this work are: 1) to determine whether the presence of $^{107}Ag^*$ in samples with high and low Pd/Ag enrichments can be attributed to *in situ* decay of extinct ^{107}Pd; and 2) to study whether the distribution of Pd/Ag in different phases and various classes of meteorites can be related to primary nebular condensation processes or is the result of later melting, metamorphism or other disturbances. The results on these samples will be used in our discussion to understand the extent to which they may reflect timescales of formation, and chemical fractionation processes in the nebula or during planetary differentiation and the physical conditions at later stage melting or break-up of the protoplanet.

2. EXPERIMENTAL PROCEDURES

Metal from samples of all iron meteorites, the two pallasites (Brenham, and Glorieta Mountain), and a mesosiderite (Horse Creek), was cut from the specimens. No macroscopic sulfides were visible in any of these dense metal samples. The metal was washed with CCl_4 and the surface was removed in three to four leaching steps with hot aqua regia to eliminate contamination to produce a central piece of shiny metal. The central piece of metal was dissolved in hot aqua regia. In the samples of chondrites, the pallasite (Eagle Station), the mesosiderites (Morristown and Emery) and a stony-iron (Bencubbin), the metal was interspersed with silicates. We did not separate metal (see later discussion). Aliquots were taken from each of the sample solutions and were spiked with ^{102}Pd and ^{109}Ag individually to determine the Pd and Ag concentrations. Unspiked aliquots were taken for Ag isotopic determination. The experimental procedures for precise Ag isotopic measurements, for eliminating mass spectrometric interferences by AsS^+ and $CaPO_2^+$ ions, and for Pd-Ag separations and analyses, are as given in *Kelly et al.* [1978] and in *Chen and Wasserburg* [1983] and in citations therein. Because of mass dependent isotope discrimination effects at the detector, care must be given to compare the results for the same detector.

3. SAMPLES AND RESULTS

The Pd and Ag concentrations and $^{107}Ag/^{109}Ag$ ratios in each analyzed sample are given in Table 1. The $^{107}Ag/^{109}Ag$ ratios were measured with either an electron multiplier detector (EM) (value shown in italics, Table 1) or a Faraday Cup detector (F). All reported ratios are "raw" data for the detector used without correcting for any mass fractionation effects. For reference, the raw ratio of $^{107}Ag/^{109}Ag$ for normal terrestrial silver is 1.0897 using the EM and 1.0811 using the F [see *Chen and Wasserburg*, 1983]. Care must be taken in comparing the shifts in $^{107}Ag/^{109}Ag$ for samples with small enrichments relative to the corresponding detector values for normal.

In a previous study of the Pd-Ag system in the metal phase of Santa Clara, *Kaiser and Wasserburg* [1983] showed that the $^{107}Ag/^{109}Ag$ ratios in the sequential leaches increase while the ^{109}Ag contents decrease from the surface to the center of the specimen. After removing ~1 mm-thickness of metal from the surface, the indigenous Ag is apparently reached, as indicated by the plateaus of both Ag contents and isotopic ratios. In this study, all metal samples were represented by these dense, shiny, central pieces.

Table 1 shows the weight of samples analyzed for the Ag isotopic composition, abundances of ^{108}Pd, ^{109}Ag, $^{107}Ag/^{109}Ag$ and $^{108}Pd/^{109}Ag$ ratios. All data were corrected for 1.2 - 2.8 x 10^{10} ^{109}Ag atoms and 2.9 - 5.8 x 10^{10} ^{108}Pd atoms analytical blanks, which usually were less than 3% of ^{109}Ag in group IVA-IVB metal samples or less than 0.5% in other samples. The blanks for Pd in the metal analyses are always less than 0.1%. Table 2 shows Pd contents, $\delta^{107}Ag$ ($\delta^{107}Ag = [(^{107}Ag/^{109}Ag)_{sample} / (^{107}Ag/^{109}Ag)_{normal} - 1] \times 1000$), $^{108}Pd/^{109}Ag$, $^{107}Ag^*/^{108}Pd$ ratios, and ΔT ("formation time difference", see discussion below) for all meteorites analyzed.

3.1. *Duchesne (IVA)*

This sample consists of an etched slab (1.1 cm x 10.5 cm x 16 cm) with two large troilite (3-5) cm nodules which appear to be free of metal. One of them occurred near the edge of the slab and was chiseled out for analysis. A detailed description of Duchesne was presented in *Buchwald* [1975].

Table 1. Palladium and Silver Abundances in Meteorites

Sample	Wt (g)	Abundance, atoms/g ^{108}Pd(10^{15})	Abundance, atoms/g ^{109}Ag(10^{11})	^{107}Ag/^{109}Ag[a]	^{108}Pd/^{109}Ag
Irons					
Duchesne Metal (IVA)	3.25	10.12±0.04	2.934±0.018	*1.9355±0.0058*	34510±244
Duchesne Sulfide (IVA)	0.43	0.0089±0.0002	12.0±0.072	1.1226±0.004	7.44±0.14
Social Circle (IVA)	3.22	4.247±0.007	2.595±0.017	*1.4863±0.0064*	16370±108
Tawallah Valley (IVB)	3.24	15.85±0.02	2.219±0.017	*2.1421±0.013*	71440±550
Klondike (IVB)	3.28	15.1±0.014	1.739±0.014	*2.5245±0.02*	86840±720
Tucson (AN)	2.8	4.598±0.009	2.624±0.019	*1.3914±0.012*	17520±132
N'Goureyma (AN)	3.32	2.026±0.003	2.577±0.017	*1.1168±0.0046*	7862±52
El Sampal (IIIA)	1.64	6.061±0.026	129.8±0.2	1.0883±0.0011	467±2
Trenton Metal (IIIA)	0.81	4.429±0.011	108.5±0.3	1.0879±0.0016	408±1.4
Trenton Sulfide (IIIA)	0.51		147.7±0.5	1.0818±0.002	
Bear Creek (IIIB)	1.06	7.704±0.047	145.5±0.7	1.0907±0.002	529±4
Mt. Edith (IIIB)	0.92	6.319±0.046	98.2±0.3	1.0946±0.0023	643±5
Chupaderos (IIIB)	0.87	8.474±0.034	153±0.7	1.0931±0.0026	554±3
Tocopilla (IIA)	1.42	2.86±0.01	83.2±0.1	1.0874±0.0006	344±1
Pallasites					
Eagle Station-1	1.35	6.725±0.024	371±1	*1.088±0.003*	181±0.8
Eagle Station-2	1.56	6.835±0.015	356.1±0.2	1.0795±0.0012	191.9±0.4
Brenham	2.15	8.867±0.014	175±0.3	1.0867±0.0007	507±1
Glorieta Mountain	2.24	8.58±0.015	159.3±0.1	1.0860±0.0012	539±1
Mesosiderites					
Morristown	2.14	5.605±0.012	285.8±0.4	1.0839±0.0006	196±0.5
Horse Creek	1.63	3.666±0.007	39.58±0.05	*1.0957±0.0017*	926±2
Emery	0.85	0.360±0.002	767±0.7	1.0809±0.0009	5.10±0.02
Bencubbin WR	3.2	0.470±0.002	288.5±0.2	1.0808±0.0016	16.3±0.1
Bencubbin Metal	0.068	4.53±0.03	200.4±0.6	1.0803±0.002	226.3±1.7
Chondrites					
Rose City (H5)	0.23	5.171±0.021	3336±3	1.0803±0.0014	15.5±0.1
Floyd (L4)	0.43	2.551±0.003	1181±1.5	1.079±0.0020	21.6±0.04

a. ^{107}Ag/^{109}Ag ratios in "italics" are electron multiplier (EM) data, otherwise, Faraday cup (F) data.

Some features in Duchesne such as Neumann bands, brecciated troilite and phosphate, and heavily faulted and fissured metal suggested that Duchesne may have been shocked prior to atmospheric entry and broken.

A chunk of metal was sawn out of the Duchesne slab in an area ~ 5 cm below the sulfide nodule. This metal appeared to be free of troilite and was analyzed following the procedures described above. The ^{107}Ag/^{109}Ag ratio measured on the metal is 1.9355±0.0058 (Table 1, EM data) which corresponds to a δ^{107}Ag value of +776±5 ‰(Table 2). The metal yielded a high ^{108}Pd/^{109}Ag ratio of 3.45 x 10^4. In a ^{107}Ag/^{109}Ag versus ^{108}Pd/^{109}Ag diagram (Fig. 2), this metal sample plots on the Gibeon isochron. The ^{107}Ag*/^{108}Pd ratio for this metal sample is 2.45 x 10^{-5} (Table 2). A chunk of troilite (2.37 g) was chiseled out and leached sequentially with the following acids (cold): 4 ml 0.5 M HBr, 4 ml 1 M HBr and 2.5 ml 12 M HCl. The resulting residue (1.73 g) consisted of an intact single piece of sulfide with a rough dark-colored surface. This piece was dissolved in 12 M HCl and hot aqua regia. The ^{107}Ag/^{109}Ag ratio in the sulfide

Table 2. Pd, $\delta^{107}Ag$, $^{108}Pd/^{109}Ag$, $^{107}Ag^*/^{108}Pd$ and ΔT in metal of meteorites

Sample	Group	Pd(ppm)	$\delta^{107}Ag$(‰)[a]	$^{108}Pd/^{109}Ag$	$^{107}Ag^*/^{108}Pd$	ΔT (my)
Chondrites						
Rose City	H5	3.45	-0.7±1.3	15.50±0.06	$<3.9 \times 10^{-5}$	< 4.5
Floyd	L4	1.7	-1.9±1.8	21.60±0.04	$<-4.6 \times 10^{-6}$	
Pallasites						
Eagle Station-1	PAL	4.48	-1.6±2.8	181.1±0.8	$<7.2 \times 10^{-6}$	<-11
Eagle Station-2	PAL	4.56	-1.5±1.1	191.9±0.4	$<-2.1 \times 10^{-6}$	
Brenham	PAL	5.91	5.2±0.7	507±1	$(1.1±0.14) \times 10^{-5}$	-7.2±1.1
Glorieta Mountain	PAL	5.72	4.5±1.1	539±1	$(9.1 \times 2.2) \times 10^{-6}$	-9.1±2.1
Mesosiderites						
Morristown	MES	3.74	2.6±0.6	196.1±0.5	$(1.45±0.33) \times 10^{-5}$	-4.7±1.9
Horse Creek	MES	2.45	5.5±1.6	926±2	$(6.5±1.8) \times 10^{-6}$	-12.3±2.3
Emery	MES	0.24	-0.2±0.8	5.10±0.02	$<1.4 \times 10^{-4}$	<16
Bencubbin	MES	3.02	-0.7±1.8	226.2±1.6	$<5.3 \times 10^{-6}$	<-14
Irons						
Canyon Diablo	IA	3.62	-0.4±1.8	43.8±0.4	$<3.7 \times 10^{-5}$	<4.0
Toluca	IA	4.5	0.0±1.5	90.5±0.3	$<1.8 \times 10^{-5}$	<-2.9
Tocopilla	IIA	1.91	5.8±0.6	344±1	$(1.83±0.18) \times 10^{-5}$	-2.53±0.88
Derrick Peak	IIB	2.35	7.2±2.8	433±3	$(1.82±0.69) \times 10^{-5}$	-2.58±3.02
Cape York #B3	IIIA	3.49	9.5±2.2	406±7	$(2.53±0.59) \times 10^{-5}$	0.51±1.97
El Sampal	IIIA	4.04	6.7±1.0	467±2	$(1.54±0.24) \times 10^{-5}$	-4.15±1.33
Trenton	IIIA	2.95	6.24±1.48	408±1.4	$(1.65±0.39) \times 10^{-5}$	-3.5±2.0
Bear Creek	IIIB	5.13	8.86±1.85	529±4	$(1.81±0.38) \times 10^{-5}$	-2.7±1.8
Mt. Edith	IIIB	4.21	12.5±2.1	643±5	$(2.11±0.36) \times 10^{-5}$	-1.2±1.5
Chupaderos	IIIB	5.65	11.1±2.4	554±3	$(2.16±0.47) \times 10^{-5}$	-1.0±1.9
Grant #836	IIIB	4.9	14.4±1.1	952±18	$(1.65±0.13) \times 10^{-5}$	-3.52±0.70
Nantan	IIICD	3.87	0.6±1.1	55.3±0.3	$<3.4 \times 10^{-5}$	<3.4
Duchesne Metal	IVA	6.74	776±5	$(3.45±0.025) \times 10^4$	$(2.452±0.023) \times 10^{-5}$	0.20±0.09
Social Circle	IVA	2.83	364±6	$(1.64±0.011) \times 10^4$	$(2.423±0.042) \times 10^{-5}$	0.09±0.16
Mart	IVA	6.43	1937±37	$(8.52±0.14) \times 10^4$	$(2.476±0.061) \times 10^{-5}$	0.29±0.23
Hill City	IVA	5.93	2423±46	$(1.005±0.02) \times 10^5$	$(2.628±0.069) \times 10^{-5}$	0.85±0.24
Bishop Canyon	IVA	3.17	890±18	$(5.15±0.086) \times 10^4$	$(1.884±0.05) \times 10^{-5}$	-2.27±0.24
Yanhuitlan	IVA	2.94	808±12	$(2.88±0.029) \times 10^4$	$(3.052±0.054) \times 10^{-5}$	2.25±0.16
Ningbo	IVA	4.29	303±3	$(1.373±0.011) \times 10^4$	$(2.405±0.027) \times 10^{-5}$	0.02±0.10
Gibeon	IVA	3.46	2570±65	$(1.141±0.028) \times 10^5$	$(2.455±0.086) \times 10^{-5}$	0.21±0.32
Tawallah Valley	IVB	10.6	966±12	$(7.14±0.055) \times 10^4$	$(1.473±0.021) \times 10^{-5}$	-4.58±0.14
Klondike	IVB	10.1	1317±18	$(8.68±0.07) \times 10^4$	$(1.652±0.027) \times 10^{-5}$	-3.50±0.15
Hoba	IVB	6.94	1680±83	$(1.042±0.06) \times 10^5$	$(1.76±0.12) \times 10^{-5}$	-2.92±1.34
Santa Clara	IVB	8.9	831±6	$(7.542±0.046) \times 10^4$	$(1.2±0.012) \times 10^{-5}$	-6.50±0.09
Warburton Range	IVB	11.6	1854±55	$(1.087±0.044) \times 10^5$	$(1.859±0.081) \times 10^{-5}$	-2.40±0.40
Tlacotepec	IVB	6.38	18.6±9.2	$(4.35±0.21) \times 10^4$	$(4.7±2.3) \times 10^{-7}$	-37±4
Tucson	AN	3.06	277±11	$(1.75±0.013) \times 10^4$	$(1.722±0.07) \times 10^{-5}$	-3.11±0.37
N'Goureyma	AN	1.35	24.9±4.3	$(7.86±0.005) \times 10^3$	$(3.447±0.59) \times 10^{-6}$	-18.2±1.5
Pinon #D	AN	12.3	964±18	$(7.41±0.25) \times 10^4$	$(1.418±0.044) \times 10^{-5}$	-4.94±0.29
Deep Spring	AN	4.32	395±18	$(6.17±0.28) \times 10^4$	$(7.0±0.4) \times 10^{-6}$	-11.6±0.6
Mundrabilla	AN	4.14	-0.2±1.7	407±1	$<3.9 \times 10^{-6}$	<-17

[a]For normal (NIST SRM 978), $^{107}Ag/^{109}Ag = 1.0897±0.0018$ (EM) and 1.0811±0.0017 (F).

residue was determined to be 1.1226±0.004 (F). This corresponds to $\delta^{107}Ag = 38.5±3.7$ ‰. The Pd content in the sulfide is a factor of 10^3 lower than the metal, and the Ag content is a factor of 4 higher. However, the $^{107}Ag^*/^{108}Pd$ ratio (0.0056) in the sulfide is a factor of 180 higher than in the metal. This demonstrates that the initial $^{107}Ag/^{109}Ag$ in

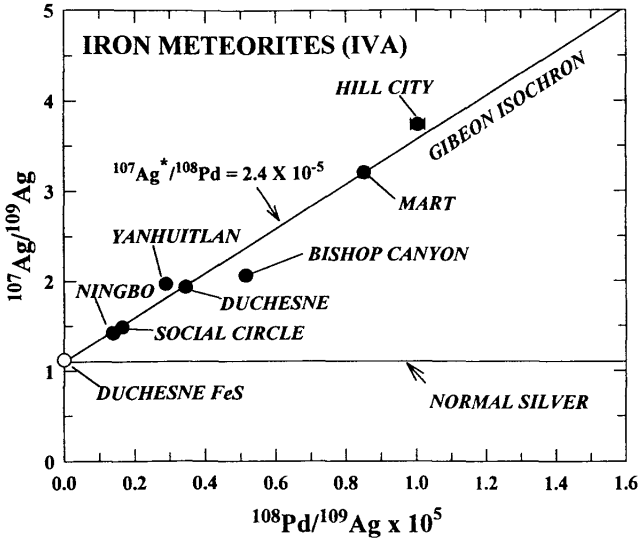

Fig. 2. Pd-Ag evolution diagram showing all IVA meteorites analyzed (metal samples), and the metal-FeS data points for Duchesne. It can be seen that all IVA samples cluster closely about the Gibeon reference isochron with departures for Hill City, Yanhuitlan and Bishop Canyon.

Duchesne is elevated or that the meteorite has been subject to metamorphism and underwent redistribution of radiogenic silver. This is similar to the results found previously for the sulfides of Santa Clara and Gibeon, both of which exhibit highly radiogenic $^{107}Ag/^{109}Ag$. The troilite data on Duchesne are plotted in Fig. 3. In this diagram, we have also shown some data from Gibeon which include 3 troilite nodules (3187, 679, and LR) and leaches on a troilite-metal contact zone (LR7-L1 and LR7-L2) from Gibeon. The $^{107}Ag/^{109}Ag$ ratios in most troilite samples from Gibeon show large $^{107}Ag^*$, but with low $^{108}Pd/^{109}Ag$. However, the leaches on the FeS-FeNi contact zone and some of the troilite nodules [see *Chen and Wasserburg*, 1990a] contain Fe-Ni metal and show high $^{108}Pd/^{109}Ag$ values (Fig. 3).

3.2. *Social Circle (IVA)*

A piece of metal free from any macroscopic troilite inclusions was cut from another group IVA iron, Social Circle (Me 2614). The results also show the presence of $^{107}Ag^*$ with $\delta^{107}Ag = 364\pm6‰$ and $^{107}Ag^*/^{108}Pd = (2.42\pm0.04) \times 10^{-5}$. These results also plot on the lower end of the Gibeon isochron (Fig. 2).

3.3. *IVB and Anomalous Irons*

Samples of group IVB iron meteorites, Tawallah Valley (Me 2705) and Klondike (Me 1963), free of any macroscopic sulfide inclusion were analyzed. Both samples show very high ^{108}Pd contents (~1.6×10^{16} atoms/g), and high $^{108}Pd/^{109}Ag$ ratios. The $^{107}Ag/^{109}Ag$ for Tawallah Valley is 2.142±0.013 and for Klondike 2.525±0.020 and are highly radiogenic. These data plot to the right of the Gibeon isochron (Fig. 4). These new results are in accord with our previous observation that there is a distinct difference between the Ag-Pd data of IVA and IVB samples.

We analyzed two samples from the anomalous (ungrouped) irons, N'Goureyma (Me 978) and Tucson (Me 858). The Tucson meteorite displays a heterogeneous mixture of metal and silicate phases that is unusual. The silicate fraction ranges from 5 to 15 volume percent, and consists of abundant forsterite, 5 μ to 3 mm in size and minor enstatite, diopside, anorthite and glass [*Buchwald*, 1975]. No macroscopic sulfides were observed in the sample studied. The Tucson sample was etched and the central piece dissolved in aqua regia. The solution containing dissolved metal and other materials was removed by centrifuging leaving a fine-grained residue of silicates. The metal sample has $^{107}Ag/^{109}Ag$ = 1.391±0.012 showing clear evidence of $^{107}Ag^*$, a high $^{108}Pd/^{109}Ag$ ratio of 1.75×10^4 and yields $^{107}Ag^*/^{108}Pd$ = $(1.72\pm0.07) \times 10^{-5}$.

The N'Goureyma sample consists of an etched slab (0.8 cm x 9.5 cm x 25.5 cm) similar in appearance to Fig. 1261 of *Buchwald* [1975]. It has the three anomalous features as described by *Buchwald* [1975]: the absence of Widmanstätten structure, dispersed distribution of fine spherical troilite inclusions and polycrystalline aggregates of inch-size taenite grains. The sample of N'Goureyma yields $^{107}Ag/^{109}Ag = 1.117\pm0.005$ (EM) which is distinctly above normal Ag and thus exhibits $^{107}Ag^*$. It has $\delta^{107}Ag$ = 24.9±4.3‰, a low $^{108}Pd/^{109}Ag$ ratio of 7862 and a very low

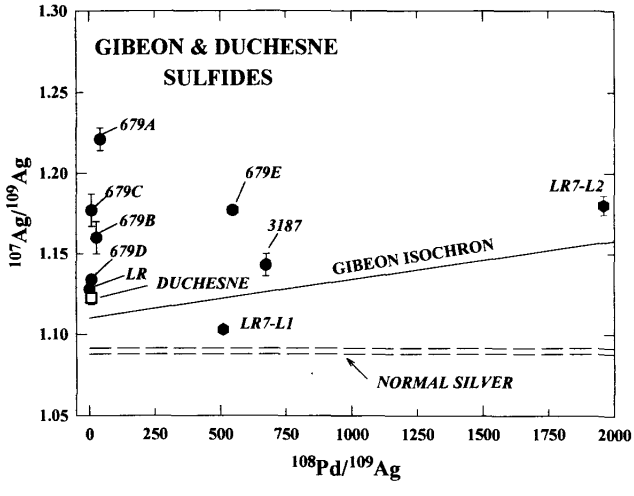

Fig. 3. Lower part of Pd-Ag evolution diagram showing the data points for FeS from Duchesne (this study) and Gibeon. Note the scatter in the data on sulfides (679A-D, LR) and metal sulfide mixtures (679E, 3187 and LR7) from Gibeon [*Chen and Wasserburg*, 1990a].

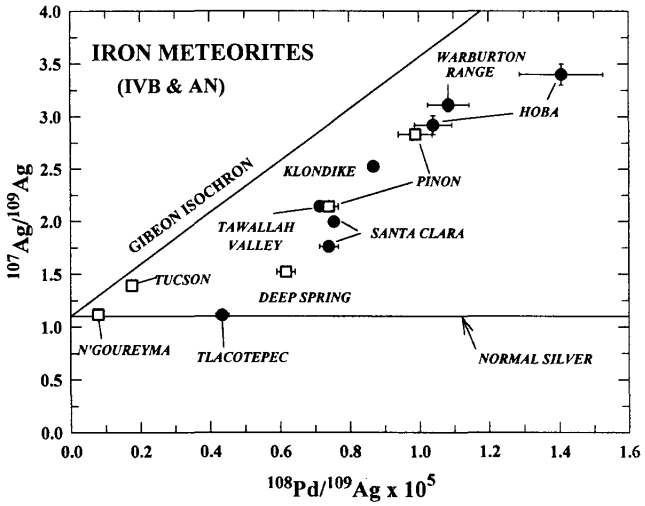

Fig. 4. Pd-Ag evolution diagram for all metal samples of IVB meteorites analyzed (solid circles) and five "anomalous" meteorites (open squares). These samples are all markedly displaced to the right of the Gibeon isochron. Note that Tlacotopec has a distinct $\delta^{107}Ag$ excess while N'Goreyma has $^{107}Ag^*$ detectable.

$^{107}Ag^*/^{108}Pd$ value of 3.45 x 10^{-6}. Both Tucson and N'Goureyma samples plot well to the right of the Gibeon isochron (Fig. 4).

3.4. *El Sampal (IIIA) and Trenton (IIIA)*

Davis and Olsen [1990] discovered excess ^{53}Cr and primordial lead in phosphates from the El Sampal meteorite. A small metal sample of El Sampal (Me 2860) free from any inclusions was provided to us by E. J. Olsen to study the Pd-Ag system. The results show $^{107}Ag/^{109}Ag = 1.0883\pm0.0011$ (F), corresponding to $\delta^{107}Ag = 6.7 \pm 1.0$ ‰. While this sample is close to normal, it exhibits a well-resolved enrichment in ^{107}Ag with $^{108}Pd/^{109}Ag = 467$ and $^{107}Ag^*/^{108}Pd = 1.54 \times 10^{-5}$. We analyzed a piece of metal from another group IIIA iron, Trenton. The metal sample contained no visible sulfide inclusions. This sample yields a $^{107}Ag/^{109}Ag = 1.0879\pm0.0016$ (F), corresponding to $\delta^{107}Ag = 6.2\pm1.5$ ‰ and a $^{107}Ag^*/^{108}Pd = (1.65\pm0.4) \times 10^{-5}$. The sulfide sample from Trenton yields a $^{107}Ag/^{108}Ag = 1.0818\pm0.002$ (F) which is the same as in normal Ag. In the Pd-Ag evolution diagram (Fig. 5), the El Sampal and Trenton data plot near an isochron with slope corresponding to a $^{107}Ag^*/^{108}Pd$ ratio of 1.5 x 10^{-5}.

3.5. *Bear Creek (IIIB), Chupaderos (IIIB) and Mt. Edith (IIIB)*

Metal samples were cut from three group IIIB iron meteorites, Bear Creek, Chupaderos and Mt. Edith, for Pd-Ag analyses. A chunk of Bear Creek metal (ASU 352.1) was leached with hot aqua regia to remove surface contamination. This sample contains a small sulfide inclusion (~ 2x4 mm^2) which was not dissolved during leaching. The leach residue consisted of a single shiny piece of FeNi containing small amounts of FeS. The Mt. Edith sample (ASU 1154) also contained a small sulfide inclusion (~ 2x7 mm^2). However, the Chupaderos (ASU 31a) metal sample contained no visible sulfide inclusions. The $^{107}Ag/^{109}Ag$ ratios are 1.0907±0.002 (Bear Creek), 1.0931±0.0026 (Chupaderos), and 1.0946±0.0023 (Mt. Edith). These values are from 8.9±1.9 ‰ to 12.5±2.1 ‰ higher than the $^{107}Ag/^{109}Ag$ ratio in terrestrial silver. The $^{108}Pd/^{109}Ag$ ratios range from 530±4 (Bear Creek) to 643±5 (Mt. Edith). In Fig. 5, we plot the new IIIB results and data from other group IIAB, IIIAB, and anomalous irons. All meteorites except Mundrabilla show small but distinctive shifts in $^{107}Ag/^{109}Ag$. There is a good correlation between $^{108}Pd/^{109}Ag$ and $^{107}Ag^*$. The sulfide data plot close to the origin with normal silver isotopic composition. All data fall between two isochrons with slopes corresponding to $^{107}Ag^*/^{108}Pd$ ratios of (I) 1.5 x 10^{-5} and (II) 2.0 x 10^{-5}.

3.6. *Tocopilla (IIA)*

The sample consisted of a small cube of pure Fe-Ni metal with no visible macroscopic sulfide inclusions. The results gave $^{107}Ag/^{109}Ag = 1.0874\pm0.0006$ (F) and a low $^{108}Pd/^{109}Ag$ ratio of 344. This corresponds to $\delta^{107}Ag = 5.8\pm0.6$ ‰. There is clear evidence of $^{107}Ag^*$. The data are shown in Fig. 5, and plot close to the data of Cape York.

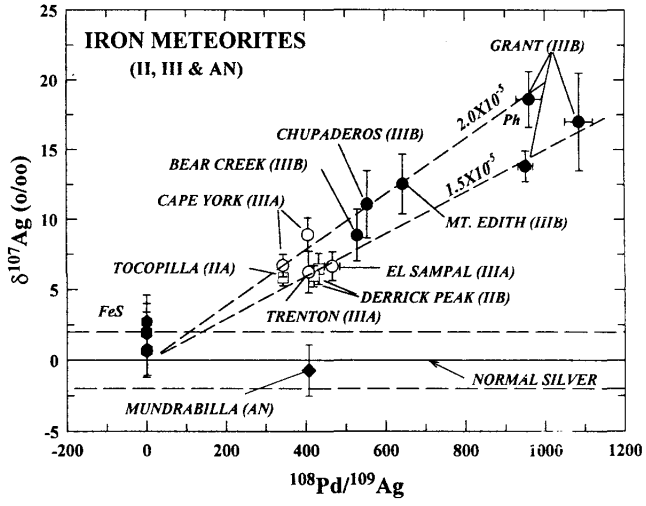

Fig. 5. $\delta^{107}Ag$(‰) vs $^{108}Pd/^{109}Ag$ diagram for data from group IIA, IIIAB and an anomalous iron. The metal and schreibersite (Ph) from all meteorites except Mundrabilla exhibit excess ^{107}Ag. The sulfides from Grant, Cape York, Derrick Peak and Mundrabilla have normal Ag and plot near the origin. These data plot between lines with a $^{107}Ag^*/^{108}Pd \sim 1.5 \times 10^{-5}$ to 2.0 x 10^{-5} and a close to normal initial $^{107}Ag/^{109}Ag$ value.

3.7. *Pallasites*

Three pallasites were analyzed. These were Eagle Station, Brenham and Glorieta Mountain. To separate metal from silicate in Eagle Station, we immersed a sample in hot aqua regia to dissolve the metal and to leave most of the silicate behind. Using this technique, we analyzed a piece of Eagle Station (#1, Table 1 and 2). The results show a normal ^{107}Ag/^{109}Ag ratio (1.088±0.003, EM) and a low ^{108}Pd/^{109}Ag ratio of 181. A second sample (#2) was analyzed and similar but more precise results were obtained. The detailed interpretation of these results are presented in a later section.

Brenham and Glorieta Mountain are members of the main group pallasite class. The Brenham specimen (Me 1272) has two distinct portions: one consisted of an aggregate of olivine and metal and the other pure Fe-Ni metal. A metal sample was sawn out of the metallic portion of Brenham and analyzed. This yielded a very high ^{108}Pd content (~9 x 10^{15} atoms/g) and ^{108}Pd/^{109}Ag ratio = 507. ^{107}Ag/^{109}Ag = 1.0867±0.0007 (F) and δ^{107}Ag = 5.2±0.7 ‰ thus exhibiting a clear ^{107}Ag* excess. The Glorieta Mountain specimen also has a large silicate-free portion, so that a few grams of pure metal could be cut for analyses. The results on the metal of Glorieta Mountain are very similar to those of Brenham and plot close together (Fig. 6). Unlike Eagle Station, Brenham and Glorieta Mountain clearly show ^{107}Ag* with a ^{107}Ag*/^{108}Pd ratio of ~1 x 10^{-5}.

3.8. *Mesosiderites*

Morristown is classified by *Powell* [1971] and *Floran* [1978] as belonging to the 3A mesosiderite group, which is one of the highly metamorphosed groups of mesosiderites. It has metal and silicate intimately intermixed. A piece (9.03 g) was dissolved in hot aqua regia for 2 days leaving a silicate residue of 3.04 g. The silicates (mainly orthopyroxene and anorthite) were left behind as a solid residue. This was undoubtedly leached by the treatment. The difference in weight of 5.99g was taken to represent the weight of dissolved metals. Aliquots were taken for Pd-Ag analyses. The results show ^{107}Ag/^{109}Ag = 1.0839±0.0006 (F) which is only slightly (~2.6 ‰) above the normal value and a low ^{108}Pd/^{109}Ag = 196. This yields a ^{107}Ag*/^{108}Pd value of 1.45 x 10^{-5} which is close to that for group II and III irons (Fig. 6).

Horse Creek is very anomalous and is not related to other known meteorites. It was classified as a "mesosiderite" by *Graham et al.*[1985]. However, a detailed description of this meteorite by *Buchwald* [1975] indicates: (1) it contains abundant nickel silicide; and (2) it chemically resembles Mount Edgerton and a number of enstatite chondrites and achondrites. A metal sample of Horse Creek was obtained that appeared to be free of any large silicate inclusions. The results show ^{107}Ag/^{109}Ag = 1.0957±0.0017 (EM) and a high ^{108}Pd/^{109}Ag ratio of 926. This yields δ^{107}Ag = 5.5±1.6 ‰

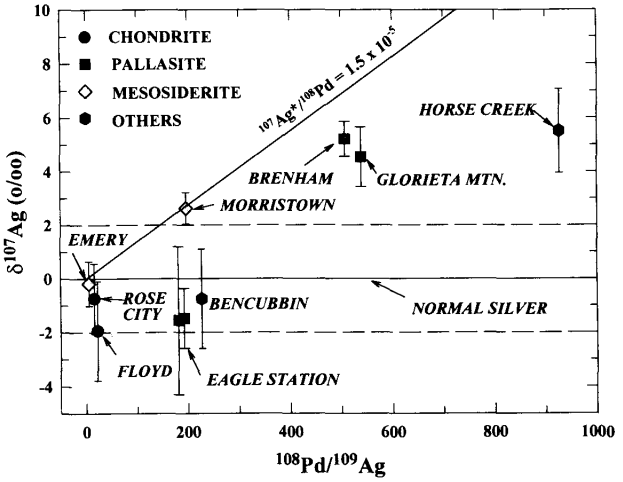

Fig. 6. δ^{107}Ag(‰) vs ^{108}Pd/^{109}Ag diagram for data from chondrites (circles), pallasites (squares), mesosiderites (diamonds) and other unusual meteorites (hexagons). The metals from Horse Creek, Brenham and Glorieta Mountain clearly show ^{107}Ag*. The metal of Morristown shows a hint of ^{107}Ag*, but it is barely resolvable from the normal silver value. Data on Rose City, Floyd, Emery, Bencubbin and Eagle Station show no detectable evidence of ^{107}Ag*.

and ^{107}Ag*/^{108}Pd = (6.5±1.8) x 10^{-6}.

Emery is classified by *Floran* [1978] as belonging to the 3A mesosiderite group. A piece (11.41 g) of Emery (Me 2645) which was intimately intergrown metal and silicate was dissolved in hot aqua regia. The solution was removed leaving a residue of 4.10 g. The difference in weight of 7.31 g was taken to be the weight of the metal dissolved. The results on Emery show normal ^{107}Ag/^{109}Ag and a very low ^{108}Pd/^{109}Ag ratio of only 5.1. The Pd content in Emery is about a factor of 14 lower than in Morristown, but Ag is a factor of 2.7 higher. It is possible that this dissolution procedure does not bring all of the Pd into solution. The results on Bencubbin discussed later indicate that a more reliable Pd content may be determined on pure metal separates.

3.9. *Other Stony Iron Meteorites*

Bencubbin is one of a few anomalous stony irons which *Kallemeyn et al.* [1978] described as a polymict breccia, consisting of a host comprised of ~60% metal and 40% ferromagnesian silicates and a selection of carbonaceous, ordinary and enstatitic chondritic clasts. Previous studies indicated that the compositions of the metal clasts of Bencubbin show elemental abundance patterns which are consistent with equilibrium condensation [*Newsom and Drake*, 1979]. The matrix material in Bencubbin is characterized by an extensive fusion texture and is believed to be the result of shock-induced melting. The shock event might only have

affected small particles surrounded by silicates, or metal adjacent to silicates and the duration of the heating event could have been very short. There is no evidence of Ni mobilization or recrystallization of chondritic fragments [*Newsom and Drake*, 1979]. The $^{15}N/^{14}N$ ratios in the silicate phases of Bencubbin are enriched by as much as a factor of 2 [*Prombo and Clayton*, 1985], and the excess ^{15}N was interpreted to be due to a nucleosynthetic origin or to extreme isotopic fractionation [*Prombo and Clayton*, 1985]. Based on this extensive information, we thought it would be an interesting candidate for Pd-Ag investigation. A piece of Bencubbin (Me 2739, USNM 5717) was analyzed by etching the whole rock sample (14.76 g) with hot aqua regia for a few days which dissolved about 55% of the total material. However, after a few days, small clusters of a black precipitate appeared in the metal-rich solution. After centrifugation, Pd-Ag analyses on aliquots of the clear solution yielded a ^{108}Pd content of 4.7×10^{14} atoms/g. This gave a low $^{108}Pd/^{109}Ag$ ratio of 16.3 and a normal $^{107}Ag/^{109}Ag$ ratio. The Pd content determined for this metal-rich phase of Bencubbin is from a factor of 5 to 20 lower than other groups of meteorites. To verify this, with some effort, we isolated and removed a single metal clast from Bencubbin. This sample was dissolved completely in hot aqua regia and no precipitates were found. The results indicate a high ^{108}Pd content of 4.5×10^{15} atoms/g, about a factor of 10 higher than the whole rock and in the same range of other irons. The discrepancy in Pd contents between the solution of the two samples may possibly be due to Pd precipitation. The cause of this difference is not clear. The metal clast from Bencubbin also gives a normal Ag isotopic composition, and a higher $^{108}Pd/^{109}Ag$ ratio of 226, similar to those in Morristown and Eagle Station.

3.10. *Chondrites*

We have extended our Pd-Ag studies to two chondrites, Rose City and Floyd, which have high iron contents. Rose City is an olivine-bronzite chondrite (H5). A piece (4.79 g) of Rose City was leached with dilute HBr, HCl and aqua regia to remove surface contamination. After leaching, the piece (4.53 g) was placed in 12 M HCl for eight days, then in hot aqua regia for one day. In this step, about 20% of the total sample was dissolved and left a residue (3.64 g) which consisted mostly of silicates. The solution contained dissolved materials from Fe-Ni metal, sulfides and some silicates (olivine). The ^{108}Pd content in the dissolved phases (mostly metal) is 5.17×10^{15} atoms/g which is within the range of most irons. This sample yielded a normal Ag isotopic composition and a low $^{108}Pd/^{109}Ag$ ratio of 15.5. We analyzed a piece (15.79 g) of Floyd (L4) using these procedures. Only a small fraction of about 1.73 g (mostly metal) dissolved. The Pd content of this material is 2.55×10^{15} atoms/g which is about 1/2 of that in Rose City. The Floyd sample yielded a normal Ag isotopic composition and a low $^{108}Pd/^{109}Ag = 21.6$. The $^{108}Pd/^{109}Ag$ ratios in Rose City and Floyd are comparable to those in group IA such as Canyon Diablo (i.e. $^{108}Pd/^{109}Ag \sim 40$), but are much lower than those in other groups of iron meteorites.

4. DISCUSSION

4.1 *Pd-Ag Systematics*

There are now sufficient data on different classes of iron meteorites to permit a general evaluation of Pd-Ag systematics. All available data on group IIA, IIB, IIIA and IIIB irons are plotted on Fig. 5. These include four FeS - FeNi pairs, Grant (IIIB), Cape York (IIIA), Derrick Peak (IIB), and Trenton (IIIA). The sulfides have very low $^{108}Pd/^{109}Ag$ ratios and the same $^{107}Ag/^{109}Ag$ ratio within limits of errors as in normal terrestrial Ag. All metal data plot close to a correlation line with a slope corresponding to a $^{107}Ag^*/^{108}Pd$ between 1.5×10^{-5} and 2.0×10^{-5}. These data appear fully consistent with a model of *in situ* radioactive decay of ^{107}Pd in meteorite parent bodies with an initial $^{107}Pd/^{108}Pd$ between $\sim 1.5 \times 10^{-5}$ and 2×10^{-5}. The close proximity of data on groups II and III irons in this diagram (Fig. 5) suggests that the relative timescales for the formation of these meteorites may be very short. Note that the degree of enrichment of ^{107}Ag is quite small for all these meteorites so that significant differences may exist and not be easily detectable. We now consider the results on Duchesne. The metal sample is highly radiogenic and a line through the sulfide yields $^{107}Pd/^{108}Pd = 2.3 \times 10^{-5}$. The sulfide shows a substantial excess of $^{107}Ag^*$. The simple interpretation of this data set is in full agreement with the model of *in situ* decay of ^{107}Pd. The only problem remaining is the elevated initial $^{107}Ag/^{109}Ag$ corresponding to an enrichment of $\delta^{107}Ag = 38.5‰$. It follows that the Ag in Duchesne must represent at least a two-stage evolution. The above cited results on Cape York (IIIA), Grant (IIIB), Derrick Peak (IIB), Duchesne (IVA) and Trenton (IIIA), are all of the existing data on metal-sulfide pairs consistent with a model of *in situ* decay.

Some previous efforts to obtain internal isochrons using sulfide and metal pairs from group IV meteorites yielded very complex results (see Introduction). With regard to the systematics of FeS and metal in a single meteorite assuming closed system behavior, we would expect that sulfides would contain excess $^{107}Ag^*$ and a higher $^{107}Ag^*/^{108}Pd$ as compared to the metal. The internal isochron of such a system should give an initial $^{107}Ag/^{109}Ag$ elevated above normal by the decay in the bulk system until such time that element exchange between metal and sulfide stopped. The shift in the initial Ag isotopic ratio should be given by:

$$\theta \equiv (^{107}Ag/^{109}Ag) - (^{107}Ag/^{109}Ag)_0 = (^{107}Pd/^{108}Pd)_\tau(\exp(\tau/\bar{\tau}_{107}) - 1)(^{108}Pd/^{109}Ag)_{WR} \quad (1)$$

where WR stands for the whole rock, $(^{107}Pd/^{108}Pd)_\tau$ is the slope of the isochron as determined today and τ represents the time required in a closed system with $(^{108}Pd/^{109}Ag)_{WR}$ to cause the shift θ. For the values $(^{107}Pd/^{108}Pd)_\tau = 2 \times 10^{-5}$ and $\tau/\bar{\tau}_{107} = 1$ one obtains $\theta = 3.4 \times 10^{-3}$ (i.e., 3‰ shift) for $(^{108}Pd/^{109}Ag)_{WR} = 100$. The behavior of such an internal isochron must give positive slopes and initial $^{107}Ag/^{109}Ag$ values greater than solar. For the case of Duchesne, this implies that the initial Ag evolved in a preceding parent system (P) for a time τ, satisfying $(\delta^{107}Ag)$ $(^{107}Ag/^{109}Ag)_\odot/(^{107}Pd/^{108}Pd)_0 \sim 2 \times 10^3 = \exp(\tau/\tau_{107})$ $(^{108}Pd/^{109}Ag)_P$. For $\tau/\tau_{107} \sim 1$, this gives $^{108}Pd/^{109}Ag \sim 10^3$ and for $\tau/\tau_{107} \sim 0.1$, $^{108}Pd/^{109}Ag \sim 2 \times 10^4$. Thus, the enhanced initial value could readily be produced over a short time by evolution in matter substantially enriched in siderophiles (e.g., an iron-nickel parent mass, possibly a planetary core). Alternatively, there is the possibility of later stage metamorphism of Duchesne itself that partially redistributed $^{107}Ag^*$ in the high bulk Pd/Ag environment of that meteorite body.

It is necessary to consider the fact that cooling is not instantaneous for iron meteorites and considerable diffusion may have taken place. For high cooling rates of 50°K/my, it would require about 12 my to cool from the melting temperature at the Fe-FeS eutectic to ~500°C. This is substantially greater than $\bar{\tau}_{107}$. For lower cooling rates of 1°K/my the time scales are long compared to $\bar{\tau}_{107}$. Recent studies indicate cooling rates range from 40° to 70° K/Ma in group IAB [*Herpfer et al.*, 1994] to 150° to 300° K for IVA [*Saikumar and Goldstein*, 1988] and to 150° to 300° K for IVB [*Rasmussen et al.* 1984]. One should thus expect that the cooling history could play a significant role in Pd-Ag systematics with regard to internal isochrons. In the subsolidus field, this depends on the relative amounts and geometrical distribution of sulfide and metal, and the diffusion coefficients of Pd and Ag which have yet to be determined for iron meteorites.

We now turn to the Pd-Ag systematics of just the bulk metal phases. Interpreting the well-defined behavior of Gibeon metal samples to represent an isochron, we may then compare this with the results on other meteorites. Note that all of the IVA meteorites, including three new results, lie close to or on the reference isochron (Fig. 2). Of these samples, we note that Bishop Canyon is displaced to the right. From the viewpoint of "total rock" analyses, it appears that six of these meteorites appear to be synchronous and cogenetic. The meteorites Yanhuitlan and Bishop Canyon appear to be distinctive but "closely" correlated. These data on IVA metal samples are strongly supportive of the hypothesis of *in situ* decay of ^{107}Pd.

We now consider the IVB irons (full circles) shown in Fig. 4. All of the data, including the new results on Tawallah Valley and Klondike, lie far to the right of the Gibeon reference isochron. The two Hoba analyses lie on a line through normal silver. The two Santa Clara points would define an almost vertical line. Tlacotepec shows a small but distinctive enrichment of ^{107}Ag [*Kaiser and Wasserburg*, 1983]. These data clearly show the presence of $^{107}Ag^*$ with a general variation of $^{107}Ag/^{109}Ag$ with $^{108}Pd/^{109}Ag$ but they do not define an isochron. These data could be interpreted as representing widely different ages. However, as pointed out by *Kaiser and Wasserburg* [1983] they appear broadly to define a line through the origin. As these workers indicated, the Pd contents are relatively constant while the normal Ag contents vary widely. Insofar as the general correlation passes through the origin, there is a suggestion that there might exist a pure ^{109}Ag component. The total array of data does not strongly support the latter hypothesis (e.g., Hoba); however, the basic reason for the observation requires attention.

In Figure 4, we have also included data on some anomalous meteorites (N' Goureyma, Tucson, Deep Spring, Piñon) all of which have $^{107}Ag^*$. These meteorites are classified as anomalous as they do not belong to either the IVA or IVB clusters based on Ga, Ge, and Ni [see *Schaudy et al.* 1972; *Wasson and Schaudy*, 1971]. All of these samples plot to the right of the Gibeon reference isochron. $^{107}Ag^*$ has also been found in two pallasites (Brenham and Glorieta Mountain), in the anomalous Horse Creek, and possibly in a mesosiderite (Morristown) with a wide range in $^{107}Ag^*/^{108}Pd$ (1.5×10^{-5} to 6×10^{-6}).

From the above observations we conclude that: 1) $^{107}Ag^*$ is present in a wide variety of iron and stony-iron meteorites; 2) it is most readily found in meteorites with a high Pd/Ag ratio; 3) it appears to be due to the *in situ* decay of ^{107}Pd in some meteorites including two phase internal isochrons and total metal isochrons; 4) the correlation of $^{107}Ag/^{109}Ag$ with $^{108}Pd^{109}Ag$ for the total metal samples of IVA,B meteorites reflects a large variation in normal silver content and a much smaller variation in Pd content; 5) there is a wide spread in apparent $^{107}Pd/^{108}Pd$ ratios; and lastly, 6) there are clear cases of complex or pathologic behavior relating to some sulfides and some metal phases (e.g. Santa Clara, Piñon and Gibeon sulfides).

4.2. *Formation Time Differences*

Assuming $^{107}Pd/^{108}Pd$ was homogeneous in the early solar system, the variations in $^{107}Ag^*/^{108}Pd$ among meteorites can be used to calculate a relative chronology using the Pd-Ag systematics. The age differences between two objects (1 and i) can be calculated from

$$\Delta T = \bar{\tau}_{107} \ln[(^{107}Pd/^{108}Pd)_i/(^{107}Pd/^{108}Pd)_1] \qquad (2)$$

When the ratios $(^{107}Pd/^{108}Pd)_i$ are established *from internal isochrons* for sample "i", then ΔT is the absolute difference in time for the fractionation of Ag and Pd in object "i" relative

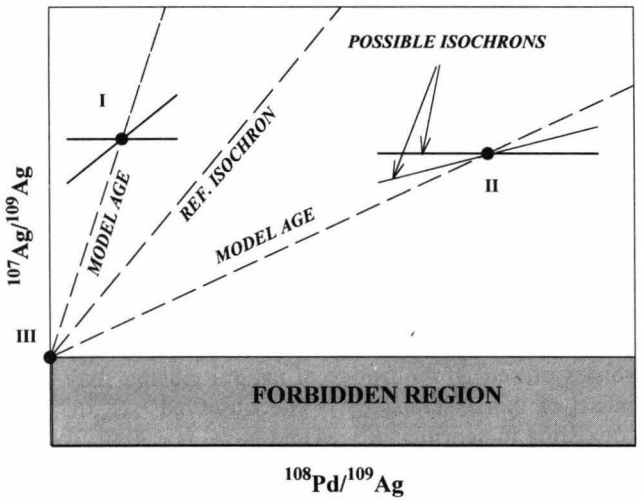

Fig. 7. A schematic diagram for Pd-Ag evolution. Points I and II represent data points above and below a reference isochron. A model age is defined by an isochron through an initial point (III) and a data point. A number of possible isochrons were also shown. See text for discussion.

to the reference 1. A relative time scale can thus be calculated between the Gibeon reference isochron and other meteorites for which there are internal isochrons. The $^{107}Ag^*/^{108}Pd$ ratio inferred from the Gibeon isochron is 2.4×10^{-5}. Only a few other samples have internal isochrons (Cape York, Grant, Derrick Peak, Duchesne and Trenton).

In the case that $(^{107}Pd/^{108}Pd)_i$ is obtained just from a metal sample (i) assuming that the initial is $(^{107}Ag/^{109}Ag)_\odot$, then ΔT is strictly a model age. If the data point $[(^{108}Pd/^{109}Ag)_i, (^{107}Ag/^{109}Ag)_i]$ lies to the right of the reference isochron (Pt. II, Fig. 7), then ΔT will be negative and is a minimum time between the formation of 1 and the last fractionation process that produced "i". If the data point lies to the left of the reference isochron (Pt. I, Fig. 7), then ΔT is the maximum (positive) time difference. In the case for very high $^{107}Ag/^{109}Ag$ and $^{108}Pd/^{109}Ag$, if one may argue that the actual initial for the sample is close to $(^{107}Ag/^{109}Ag)_\odot$, then the model age is close to the true time difference. The calculated ΔT values using only the metal data are given in Table 2 for all available data and are plotted against Ge contents in Fig. 8. These data indicate that the range in ΔT for group IVA irons is very small (±2.25 my). ΔT for other groups of meteorites have negative values (i.e., younger than Gibeon). The total range in ΔT for all meteorites where $^{107}Ag^*$ was detected is ~39×10^6 y.

In discussing these model ages, we must consider the basic question of what chemical fractionation processes and events govern the Pd-Ag chronometer. Assuming an initial state of the solar system with fixed $^{107}Pd/^{108}Pd$ and $^{107}Ag/^{109}Ag$ ratios, the issue is what the processes are that will fractionate or sequester the parent and daughter elements. It is evident from the considerations of *Kelly and Larimer* [1977] that the first stages of a condensation process will cause large enrichment of Pd over Ag in the Fe-Ni metal phase that forms. A sequence of such metal condensates, if isolated, would then have $^{107}Pd/^{108}Pd$ that was a direct reflection of the times of condensation. The silicates and sulfides which form later in such processes of sequential condensation would have such low Pd/Ag ratios ($(^{108}Pd/^{109}Ag)_\odot \approx 1.6$) as to obscure any effect from ^{107}Pd decay. To observe an effect at the level of 2‰ would require an enrichment in Pd/Ag relative to solar of a factor of 60. As for a given mass of metal phase or metal-sulfide mix that remains a closed system, repeated melting will not alter the bulk system $^{107}Pd/^{108}Pd$ ratio in its initial state from the values of $^{107}Ag^*/^{108}Pd$ in its final state today. However, a planetary object is a mixture of metal, FeS and silicates. It will have a different behavior when it is melted and then subject to macroscopic physical separation of Pd and Ag within that body. Hence, any chronometer of "bulk" meteorites must depend on the physical separation and removal of parent and daughter elements within the planetary body. In all subsequent discussion the various possible time meanings and their connection with processes should be kept in mind when considering the broader implications.

Let us first consider the extreme case for Ag-Pd separation by assuming that an *ad hoc* phase X quantitatively segregates all Ag in a system. If phase X is originally present in this system and is then totally removed from the system at a time 0, then the remaining system will have no ^{107}Ag and no ^{109}Ag. A growth of purely radiogenic ^{107}Ag will then

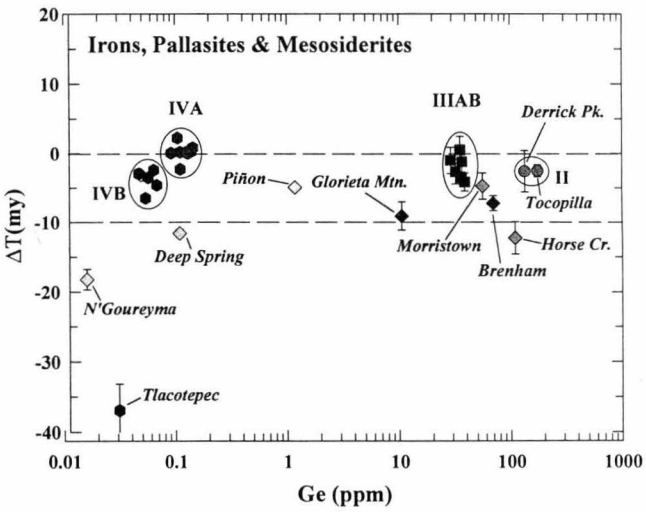

Fig. 8. ΔT(my) versus Ge (ppm, log scale) for all meteorites which show the existence of $^{107}Ag^*$. The difference in time interval of formation (ΔT) was calculated relative to a $^{107}Ag^*/^{108}Pd = 2.4 \times 10^{-5}$ as defined by the Gibeon isochron. Most samples from various classes lie within a narrow time bound but two samples show much younger model ages. ΔT values for groups are small.

follow. If the system subsequently remains isolated, then the final state will have $(^{107}Ag^*/^{108}Pd)_\infty = (^{107}Pd/^{108}Pd)_0$ and $^{107}Ag/^{109}Ag = \infty$ after the decay of ^{107}Pd. If, however, at some intermediate time t, some additional amount of phase X is added to the system, equilibrated and then removed, the clock is restarted and the final state will be $^{107}Ag^*/^{108}Pd = (^{107}Pd/^{108}Pd)_0\ e^{-t/\tau_{107}}$. Such a behavior would remove any connection of the Pd-Ag systematics with ^{109}Ag as it is completely stripped from the system in this model. This is a highly oversimplified model without a strong physical-chemical basis, but it focuses sharply on the issues.

If we consider this "phase X" to be the essential reason for the observed Pd-Ag systematics, particularly in IVA and IVB meteorites, then one must conclude that essentially all of the normal silver measured in these meteorites (~ 4 x 10^{11} atoms/g) is due to contamination. This would explain the effects discussed by *Kaiser and Wasserburg* [1983] where ^{109}Ag appears to be independent of Pd and $^{107}Ag^*$ and the isochrons are due to Pd and purely radiogenic ^{107}Ag with no ^{109}Ag. This would not readily explain the $^{107}Ag/^{109}Ag$ in the Santa Clara sulfide which lies above that of the associated metal. For meteorites with extremely low Ag concentrations, a possible explanation of the observations is that the sulfide and metal contained almost pure $^{107}Ag^*$ and that they were then contaminated on the earth. The number of normal Ag atoms per gram that must be added to the sulfide is much greater than for the metal so that the sulfide may retain a more elevated value. We recognize this is an *ad hoc* explanation.

We will now assume that sulfide-metal separation is the governing fractionation mechanism and will assume that the distribution coefficients of Ag for sulfide relative to metal satisfy $C_{Ag}^{Sulfide}/C_{Ag}^{Metal} \equiv K_{Ag} \gg 1$. The observed values of K_{Ag} will be discussed later. To change the $^{107}Ag/^{108}Pd$ ratio in a bulk metal, metal-sulfide assemblage requires that Ag or metal be separated from the system. It follows that variations in the $^{107}Ag^*/^{108}Pd$ ratio and hence in the model age relative to normal $^{107}Ag/^{109}Ag$, are related to the time of removal of Ag from the system by the carrier phase. In this case, the model ages using the metal samples refer to a time scale between that of the reference state (1) and the time of remelting. The model ages ΔT, given in Table 2, then reflect some blend of planetary reprocessing timescales and solar nebular time-scales. We note that the remelting of a metal-sulfide mass that has a high Pd/Ag ratio should produce FeS masses with highly radiogenic Ag and very high $^{107}Ag^*/^{108}Pd$ ratios. If these sulfides were then physically removed, they would contain highly radiogenic Ag. No such isolated sulfide meteorites have yet been found. The possibility of sulfide meteorites has been postulated by *Wasson* [1985] on other grounds. From this point of view, the displacement of the IVB data to the right of the Gibeon line would be interpreted as effected by the time of removal of sulfides (containing $^{107}Ag^*$) from an original metal-sulfide mass due to a melting-remelting process.

The extent to which the sulfide can perform the miracle required of phase X is not, in our view, reasonable in light of the observations of distribution coefficients on natural materials [*Chen and Wasserburg*, 1990a]. The limited available experimental data obtained by *Jones et al.* [1986; 1993] indicate that Ag is more compatible in the metal than in FeS and is in conflict with the observations on natural systems. In our subsequent discussion we will use the data on natural systems. The matter of the effective distribution coefficients between sulfide and metal requires resolution by more refined laboratory experiments with the appropriate chemistry. As Jones suggested, it is possible that minor phases present in the troilite of natural systems may be the cause of this discrepancy. The observed C_{Ag}^{FeS}/C_{Ag}^{Fe} in coexisting meteoritic sulfides and metal is ~ 4-40. We will use a nominal value of 20. For a bulk system (solar mix) with Fe not oxidized, the ratio by weight of FeS/Fe ~ 0.66. If K_{Ag} ~20, then ~7.0% of the total Ag would be in the metal phase. For a more reasonable estimate of FeS/Fe ~ 0.1 in a planetary core, then 33% of the Ag would be in the metal phase. It follows that to remove Ag effectively from the metal would require multiple extractions with the repeated addition of Ag-free FeS to the system. If this is correct, it is not possible to use FeS as an extremely efficient phase for the removal of Ag. However, sulfide removal could reasonably explain changes in Pd/Ag of a factor of 2 to 10.

The group IVB irons are enriched in refractories and depleted in volatiles. From considering several elements, *Kelly and Larimer* [1977] showed that metal in group IVB matches that predicted for the metal condensate at 1270°K, implying metal condensation and accretion at high temperatures. The metal in group IVA is also depleted in the most volatile elements (Ga and Ge), indicative of either a high condensation temperature (>1200°K) or a small admixture (~1%) of volatile-rich material [*Larimer and Anders*, 1967]. The ΔT values on group IVA and IVB irons do not support the prediction that group IVB irons condensed earlier and at higher temperatures. Instead, ΔT for IVB irons are very restricted (from 0 to 6.5 my younger) with the exception of Tlacotepec (see Fig. 8 and Table 2) which is the youngest by far. The small range in ΔT values for group IVA suggests that they were isolated from the nebula within a relative short period of time and formed in a single core or several cores.

The ΔT for pallasites (Brenham and Glorieta Mountain) indicate that they were formed or rather underwent Pd-Ag fractionation after the IVAs, most of the IVBs, and the IIA,B, IIIA,B meteorites. The Ir and Ni contents of pallasites [*Wasson and Kimberlin*, 1967; *Wasson*, 1974] place the majority of them near the Ni-rich end of group IIIAB. Similarly, the pallasites plot near IIIABs with high Ni in a Pd-Ni diagram (see Fig. 9). This would be consistent with the metal having been the last to crystallize, presumably near a core-mantle boundary. This agrees with our model based on ΔT but we note that the time differences appear to be less than

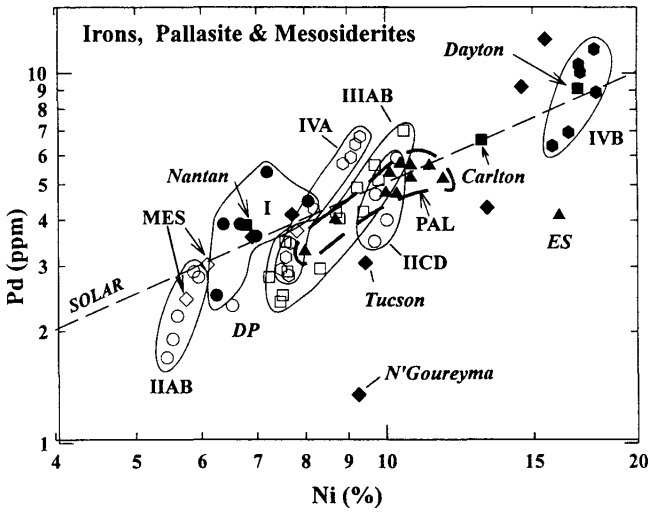

Fig. 9. Pd (ppm) versus Ni (%) diagram (both in log scales) for iron meteorites and other meteorites. The symbols are: closed circles=IA; open circles=IIAB (DP=Derrick Peak) and IICD; open squares=IIIAB; closed squares=IIICD (Nantan, Carlton and Dayton); open hexagonals= IVA; closed hexagonals=IVB; triangles=pallasites; open diamonds =mesosiderites; closed diamonds =ungrouped. The fractionation of Pd relative to Ni is very limited. Within the groups IIAB, IICD, IIIAB, IVA, and IVB Pd and Ni show good positive correlations. A straight dashed line represents the ratio of the solar abundance of Pd to Ni. Most meteorite groups generally plot along this line, but within each group the trend line defines a different Pd/Ni ratio. Note that all AN meteorites also seem to fit a trend line which fills the gap between IICD and IVB.

~ 10 my. The Ni, Ga, Ge and Ir contents of mesosiderites [*Wasson et al.*, 1974] place most of them in a cluster close to group IAB, suggesting a similar origin. As noted later, we would put them in a "cluster" with the II and III classes, and with a close, but lesser, affinity with IAB. The absence of $^{107}Ag^*$ in Emery (which has low Pd/Ag) gives a very high upper limit of $^{107}Ag^*/^{108}Pd < 10^{-4}$, or $\Delta T \lesssim 16$ my. The small $\delta^{107}Ag$ indicates the presence of $^{107}Ag^*$ in Morristown which has ΔT = -5 my. However, *Prinzhofer et al.* [1992] showed that Morristown yielded a younger Sm-Nd age of 4.47 Æ while preserving clear evidence of ^{146}Sm. The mesosiderites have surely undergone multistage metamorphism [see *Stewart, Papanastassiou and Wasserburg*, 1994]. It is conceivable that we have seriously underestimated the error in our Ag isotopic measurements. The most plausible explanation is that the bulk metal in Morristown was enriched in Pd/Ag early enough to contain ^{107}Pd. At a later time ($\lesssim$ 4.47 Æ ago), the meteorite parent body was reheated to high temperature to partly reset the ^{147}Sm-^{143}Nd systematics but the metal retained most all of its $^{107}Ag^*$. This would require that ^{107}Ag did not get redistributed to the silicate phase. Considering the stability of ultra low levels of Ag in FeNi metal, and the absence of other abundant phases that could serve as a sink for Ag, we consider this resilience of the Pd-Ag system to be quite reasonable. We also obtained ΔT on iron meteorites that do not belong to any other well-defined group (i.e., anomalous). Except for Mundrabilla which is rich in sulfides (approaching the solar FeS/Fe ratio), all of them definitely show the presence of $^{107}Ag^*$ and have a wide range of ΔT (-3.1 to -17.0 my).

4.3 *The Cosmochemistry of Pd and Ag and the Formation of Iron Meteorites with High Pd/Ag*

Wasson and colleagues [*Wasson*, 1967; *Wasson and Kimberlin*, 1967; *Wasson*, 1969, 1970a,b; *Wasson and Schaudy*, 1971; *Schaudy et al.*, 1972; *Scott et al.*, 1973; *Scott and Wasson*, 1975; *Kracher et al.* 1980; *Malvin et al.* 1984] resolved a few chemical groups of iron meteorites based on Ga, Ge, Ir and Ni contents. These elements are strongly siderophile but differ in volatility. Therefore, variations in the volatile element contents may reflect time differences in condensation and formation of the planetesimals in different part of the solar nebula. In Fig. 8 we plot the values of ΔT against the Ge contents [from *Wasson*, 1974]. It is evident that there is no correlation between ΔT and the Ge contents. Most all samples lie within a narrow band of ΔT with only two major exceptions (N'Goureyma and Tlacotepec). If the variations in $^{107}Ag^*/^{108}Pd$ correctly indicate age differences, then the Ge content in iron meteorites does not correspond to a time sequence. The most remarkable result that can be seen in Fig. 8 is that the IVA, IVB, IIIA, IIIB, IIA, IIB meteorites lie within a very narrow time zone (within a band of ~ 12 my). This same time zone includes two pallasites, two mesosiderites and three anomalous meteorites. It appears that a wide variety of irons and iron-silicates formed within about 12 million years. Some meteorites of the same groups (N'Goureyma and Tlacotepec) formed or underwent Pd-Ag separation much later (up to 37 my).

In Figure 9, we have plotted the concentrations of Pd against Ni on log scales and have employed different symbols for each group. The Ni data are from *Wasson* [1974] and *Wasson et al.* [1974]. The Pd data are from our work and from *Mermelengas et al.* [1979] also using the IDMS technique. The appearance of the Pd-Ni plot in Fig. 9 is generally similar to that reported by other workers based on Pd data determined by the neutron activation technique [cf *Scott*, 1972]. Note that the fractionation of Pd relative to Ni is very limited. A straight dashed line represents the ratio of the solar abundance of Pd to Ni, where $(Pd/Ni)_\odot = 5.1 \times 10^{-5}$ by weight. Samples from most iron groups, as well as pallasites and mesosiderites, generally plot along this solar abundance line. One anomalous iron, N'Goureyma, plots far below this line. Within each of the groups, IIAB, IICD, IIIAB, IVA, and IVB, the Pd and Ni data show good positive correlations. The envelope for each of these groups appears to define elongated trends that are nearly parallel to each other and cut across the solar ratio line. The cause for these apparent

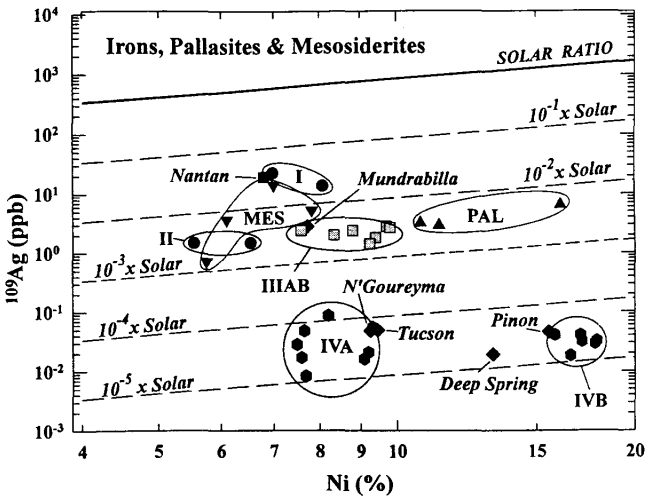

Fig. 10. ^{109}Ag (ppb) versus Ni (%) diagram (both in log scales) for iron meteorites and other meteorites. There is no correlation between Ag and Ni. All groups of meteorites plot below the straight line which represents the solar abundance ratio. The dashed lines represent different degrees of depletions of Ag/Ni. Groups IVA and IVB, as well as AN, are very depleted in Ag relative to Ni.

trends in a Pd-Ni plot and other elements against Ni plots have been discussed in several previous papers [cf *Scott*, 1972; *Kelly and Larimer*, 1977].

Scott [1972] pointed out that at least two processes must be involved to explain the fractionations between groups and within each group of iron meteorites. According to Scott, these are (1) fractionation during condensation and accretion of the solar nebula, (2) fractionation between metal, silicate and sulfide phases in the parent bodies, and (3) fractional crystallization of a liquid iron core. The correlations between trace element and Ni contents within a group could be explained by fractionation between solid and liquid during crystallization. A few experimentally determined liquid-crystal partitioning data are available for the Fe-Ni system [*Jones and Drake*, 1983; *Malvin et al.*, 1986]. The effects of adding nonmetals (S and P) to the Fe-Ni system and the segregation of trace metals during solidification of Fe-Ni-S, Fe-Ni-P and Fe-Ni-S-P alloys have been discussed by *Jones and Malvin* [1990]. However, no such data exists for Pd and it can only be estimated from the available phase diagrams [*Scott*, 1972]. The estimated distribution coefficient for Pd between γ-Fe and liquid is less than one, in agreement with the positive correlations observed between Pd and Ni within each group. From this we can surmise that the residual liquid would be enriched in Pd. *Kelly and Larimer* [1977] discussed the physical-chemical history of the metal phase from condensation and accretion to processing in the parent bodies. Some of these processes will be discussed in the following sections. Figure 10 shows the log(^{109}Ag) concentration of all the samples analyzed versus the log Ni concentration. These data are for "metal" samples. For reference, a line with the solar ^{109}Ag/Ni ratio [$(^{109}Ag/Ni)_\odot$ = 8.8 x 10^{-6} by weight] is shown. It can be seen that there is an enormous range in ^{109}Ag/Ni. The group I meteorites are around 4 x 10^{-2} x $(^{109}Ag/Ni)_\odot$. We note that Nantan, a IIICD meteorite containing primordial Pb, plots within the group I samples on both Figs. 9 and 10, suggesting an affinity with group I. The groups IIA,B, IIIA,B and three pallasites lie in the neighborhood of 4 x 10^{-3}x$(^{109}Ag/Ni)_\odot$. In addition, three pallasites lie in this same region. Note that Mundrabilla lies in the region occupied by the IIIABs in both Figs. 9 and 10. The mesosiderites range from 1.4 x 10^{-3} to 3 x 10^{-2} x $(^{109}Ag/Ni)_\odot$. The IVA and IVB meteorites lie between 1.2 x 10^{-5} to 1.2 x 10^{-4} x $(^{109}Ag/Ni)_\odot$ and are displaced far below all other meteorite classes. Four anomalous meteorites (N'Goureyma, Tucson, Deep Springs and Piñon) lie in this range. This behavior is completely different from that of Pd-Ni shown in Fig. 9. We define, from Fig. 10, this region of very high Ag depletion as VDM (volatile depleted metal) meteorites. This includes the above listed "anomalous" meteorites. It is evident that all of these different meteorite classes have ^{109}Ag/Ni below solar, that they appear to define groups and that some groups are extremely far below the solar values (e.g., VDM irons). The definition of VDM meteorites based on Ag/Ni is in accord with the view of *Kelly and Larimer* [1977] and *Scott and Wasson* [1975] that they are highly depleted in other volatile elements (e.g., Ga, Ge, Sb and P). In addition, Cu and Au are also very depleted in group IVB irons.

A condensation process such as envisaged by *Kelly and Larimer* [1977] could provide an initial system very highly enriched in Pd relative to Ag. In this case, we must attribute the extreme chemical fractionation process to an early stage of condensation and isolation of FeNi to form planetary bodies. Early condensation and segregation has many of the properties attributed to "phase X" in the previous discussion. The simplest model is one where Fe-Ni rich material formed by condensation at elevated temperatures. If this metal is segregated and then aggregated in planetary bodies, it will thus be depleted in volatiles (e.g., VDM meteorites). Some of these planetary bodies could also contain or aggregate a small amount of material not greatly depleted in all volatiles. It thus might contain a small complement of FeS which was very low in Ag. If subsequently some of these bodies were remelted with removal of FeS (now with some Ag), they thereby would give younger ^{107}Pd-^{107}Ag ages (IVB, Piñon, Deep Springs, Tucson, N'Goureyma). To remove ~1/2 of Ag from metal to sulfide would require only about 4.8% FeS in the total system (if K_{Ag}=20). The sulfides thus removed should exist in other meteorites and should contain ^{107}Ag*. Other meteorites which were formed from materials from more diverse condensation regimes and are relatively rich in volatiles (e.g.,

group I), would show much smaller degrees of Pd/Ag enrichment. In these cases, the major (but much smaller) Ag-Pd separation is most reasonably due to the enhancement of FeS-FeNi separation on planetary bodies with only a minor effect of fractionation due to the presence of early (i.e., high temperature) condensates in these objects. The PGE would, in any event, be highly enriched in the FeNi metal phase. For the case of the IIAB, IIIAB and pallasites, we would appeal to parent bodies that were a mixture of high-temperature condensates and substantial material rich in volatiles. Alternatively, these could represent an intermediate stage of condensation where some substantial enrichment of Pd over Ag has occurred, but not as extreme as in the case of VDM meteorites.

In this discussion, it is apparent that there is a basic problem in relating the meteorites to condensation processes of FeNi, of Pd, to FeS formation and to the mechanism of Ag removal during condensation. An excellent summary of the condensation sequence from a gas of solar composition and the possible relationship with various meteorites is given by *Grossman and Larimer* [1974]. Their presentation discusses a large number of chemical elements and considers equilibrium between condensates and the remaining gas phase. The result of a particular evolutionary trend depends upon the extent to which condensed materials might be isolated from the gas phase or if gas-solid equilibrium is only partially achieved.

We consider that Pd and Ag are not affected by the presence of condensed silicates and oxides and will focus on metal and sulfide formation. The elements Os, Re and Zr condense out well before Ni or Fe (~1375°K). These refractory siderophile elements are presumably included by and dissolved in the later-formed FeNi metal. Ge condenses out somewhat after Fe-Ni followed by Pd. There is a gap of about 300°K between FeNi condensation and the condensation of Ag metal. Troilite becomes stable at the much lower temperature of 700°K. If Os and Re are dissolved in FeNi metal, then the continued condensation of FeNi would dilute the concentration of very refractory PGE which condensed earlier. However, the lower condensing Pd would not follow such a trend if it all dissolved in FeNi, but its concentration would be more or less constant [cf *Kelly and Larimer*, 1977]. This Pd would have to react with the somewhat earlier condensed FeNi and could, in fact, be enriched in late forming metal. Ag begins to condense at 1000°K and would be completely condensed at 800°K far before the formation of FeS. As a result, Ag condensation is not related to sulfur. The FeS that forms is produced by H_2S (g) - Fe (m) reaction. This should be essentially Ag free and thus could provide pure FeS (without Ag). Such a process requires separation of Ag metal from the remaining nebular gases as discussed earlier. The mechanism of sequestering such intermediate condensates is not evident. If such an approach is followed, the important question is: where is the "moderately volatile" Ag during a sequential condensation process? It could be in solid solution in Cu metal which condenses out about 150°K below iron. This Cu would also have to be removed from the system and could also contain some Pd. We consider that a scenario along these general lines is required. The details of Ag condensation and segregation then become the key issue. From the point of view presented above, we must infer that the chalcophile character usually attributed to Ag from a cosmochemical point of view is only operative during planetary stages where FeS has already formed or in the cool or late nebular stage after pre-existing Ag-containing phases react with H_2S. We believe our scenario is in general accord with the proposals by *Larimer and Anders* [1967] and *Wasson and Chou* [1974] and *Wai and Wasson* [1977], who have interpreted volatile element patterns in chondrites in terms of separation and accretion during condensation.

Some of the Pd-Ag redistribution on a local scale in meteorites may involve subsolidus and diffusive effects during parent planet cooling, but we believe that the dominant processes in those meteorites relatively rich in volatiles must be due to larger scale melting and sulfide separation. A better resolution of this issue will depend on laboratory determination of distribution and diffusion coefficients with consideration of minor elements and phases that may serve as carriers. It will also be necessary to try to establish even stricter limits on terrestrial contamination of Ag in Fe-Ni metal than have heretofore been achieved.

Another important short-lived nuclide that is plausibly related to the formation of iron meteorites is ^{60}Fe ($\tau_{60} = 2.1 \times 10^6$ y). Evidence for the presence of ^{60}Fe through the increase in ^{60}Ni correlated with Fe was discovered by *Shukolyukov and Lugmair* [1993a] in the eucrite Chervony Kut. Further evidence was found in Juvinas [*Shukolyukov and Lugmair*, 1993b]. These basaltic meteorites are highly depleted in Ni relative to Fe, most plausibly due to differentiation on planetesimals during the process of metal-silicate segregation. This process greatly decreases the Ni content of the silicate. The short mean-life of ^{60}Fe (1/4 times that of ^{107}Pd) requires that the time scale for planetary formation subsequent to the collapse of the solar nebula be short. It has not yet proven possible to establish a reliable chronometric character to this nuclide [see *Shukolyukov and Lugmair*, 1993b; *Lugmair, Shukolyukov and MacIsaac*, 1994]. Indeed, more extensive data sets on ^{60}Fe-^{60}Ni consistent with isochrons are required. Nonetheless, it appears that a time scale of ~ 5 x 10^6 y between late-stage nucleosynthesis and planet formation is plausible. This is consistent with values obtained for an AGB source of ^{26}Al, ^{107}Pd, ^{60}Fe and ^{41}Ca [*Wasserburg et al.*, 1995]. This is also compatible with the relative range in model ages for many meteorites as summarized here. We note, however, that the ^{107}Pd-^{107}Ag data from several iron meteorites summarized here demonstrate that the

Table 3. A comparison between ^{107}Pd and ^{53}Mn data on meteorites.

Sample	$^{107}Ag^*/^{108}Pd$	$^{53}Cr^*/^{55}Mn$	Phase[a]	Reference[b]
Cape York (IIIA)	(2.53 ±0..59) x 10^{-5}	(2.2±1.0) x 10^{-5}	Ph	1,2
El Sampal (IIIA)	(1.54±0.24) x 10^{-5}	(8±1) x 10^{-7}	Ph	4,2
Grant (IIIB)	(1.65±0.13) x 10^{-5}	(1.0±0.4) x 10^{-6}	Ph	1,2,3
Bear Creek (IIIB)	(1.81±0.38) x 10^{-5}	(2.4±0.2) x 10^{-6}	Ph	4,5
Mt. Edith (IIIB)	(2.11±0.36) x 10^{-5}	(2.4±0.2) x 10^{-6}	Ph	4,5
Chupaderos (IIIB)	(2.16±0.47) x 10^{-5}	(2.4±0.2) x 10^{-6}	Ph	4,5
Eagle Station (Pal)	<7.2 x 10^{-6}	(2.3±0.3) x 10^{-6}	Ol	6
Springwater (Pal)	-	(1.4±0.4) x 10^{-5}	Ph, Ol	2
Brenham (Pal)	(1.1±0.14) x 10^{-5}	-	-	4
Glorieta Mountain (Pal)	(9.1±2.2) x 10^{-6}	-	-	4
Mundrabilla (AN)	<3.9x 10^{-6}	<1.5 x 10^{-7}	MnS	4,5
Toluca (IA)	<1.8 x 10^{-5}	<5 x 10^{-8}	MnS	4,5

[a]Phases analyzed for Cr/Mn: Ph = phosphate, O = olivine, MnS = alabandite.
[b]1 = *Chen and Wasserburg* [1983]; 2 = *Hutcheon et al.* [1992a]; 3 = *Kaiser and Wasserburg* [1983]; 4 = this report; 5 = *Hutcheon et al.* [1992b]; 6 = *Birck and Allègre* [1988].

planetary differentiation processes must have extended over a period of substantially greater than 10 my.

4.4 *Comparison between ^{107}Pd and ^{53}Mn*

Strong evidence for the presence of ^{53}Mn (τ = 5.3 x 10^6 y) in the early solar system was found by *Birck and Allègre* [1988]. As this lifetime is much longer than that of ^{26}Al (τ=1.05x10^6y), it is expected that ^{53}Mn would be present in planetary materials. Some evidence was found for ^{53}Cr excesses in olivine from the Eagle Station, showing a small effect of δ^{53}Cr = 1.7 ‰ [*Birck and Allègre*, 1988] with $^{53}Mn/^{55}Mn$ = 2.3 x 10^{-6}. *Davis and Olsen* [1990] found a large ^{53}Cr excess of δ^{53}Cr = 31 ‰ in phosphate from El Sampal (IIIA) and inferred an initial $^{53}Mn/^{55}Mn$ of ~ 5 x 10^{-7}. Recently, *Hutcheon et al.* [1991, 1992] analyzed Cr isotopic compositions in several iron meteorites, including Cape York and El Sampal, and a pallasite (Springwater) and found clear evidence of $^{53}Cr^*$.

Several group IIIAB irons, Bear Creek, Chupaderos, Mt. Edith and Sandtown exhibit well-defined correlations between $^{53}Cr^*$ and Mn/Cr and yield $^{53}Cr^*/^{55}Mn$ = (2.4±0.2) x 10^{-6} [*Hutcheon et al.*, 1991]. These workers also showed that silica-phosphate and olivine in the Springwater pallasite give well-resolved $^{53}Cr^*$, and with data from troilite, define a linear array with a slope $^{53}Cr^*/^{55}Mn$ = (1.4±0.4) x 10^{-5}. We summarize all existing data on ^{107}Pd and ^{53}Mn from iron meteorites and pallasites in Table 3. The only samples so far reported where these two short-lived isotopes can be compared are shown in Fig. 11. Only upper limits exist for Eagle Station, Mundrabilla and Toluca. For two samples of Eagle Station $^{107}Ag^*$ was not detected. For sample #1, using the upper limit for the experimental result and assuming the average $(^{107}Ag/^{109}Ag)_\odot$ for the multiplier, we obtained a $^{107}Ag^*/^{108}Pd$ < 7.2 x 10^{-6}. Examining the more precise Faraday cup detector value for sample #2 we would not argue for any $^{107}Ag^*$ if the uncertainties in normal are ignored. In contrast, Eagle Station has a reported $^{53}Cr^*/^{55}Mn$ = 2.3 x 10^{-6}. The samples, Cape York, Grant, El Sampal, Chupaderos, Bear Creek and Mt. Edith, all have clear evidence for both $^{107}Ag^*$ and $^{53}Cr^*$. These samples have a narrow range of $^{107}Ag^*/^{108}Pd$ [(1.5 - 2.3) x 10^{-5})] whereas the range of $^{53}Cr^*/^{55}Mn$ is from 8 x 10^{-7} to 1.8 x 10^{-5}. All of these samples yield the same ΔT to within 5 x 10^6 y. This time difference would only produce a shift of a factor of 2.5 in $^{53}Mn/^{55}Mn$ ratio. In contrast, the observed $^{53}Cr^*/^{55}Mn$ are different by a factor of 22. The major conflicts exist between Cape York, Eagle Station and the five other meteorites.

It follows that there are serious discrepancies between the two systems (see Fig. 11). The time trajectories, assuming the initial states were defined by Cape York, Mt Edith, and Chupaderos, are shown in the figure. These trajectories are not compatible with an initial state with uniform $^{53}Mn/^{55}Mn$ and $^{107}Pd/^{108}Pd$. The discrepancies could be explained by appealing to redistribution of ^{53}Cr during slow cooling, or the late formation of phosphate (by ~20 x 10^6y). In contrast to the microscopic phases exhibiting $^{53}Cr^*$, and the several phases that contain both Mn and Cr, the ^{107}Pd and $^{107}Ag^*$ appear to be almost exclusively in the metal phase and thus cannot be readily redistributed. This is an appealing hypothesis. Considering only the Pd-Ag data on Eagle Station, sample #1, the upper bound lies on the closed-system decay curve of Cape York after ~12 my from a source with the same initial ^{53}Mn and ^{107}Pd as in the parent body of Cape York. The precise bounds on $^{107}Ag^*$ for Eagle Station are critically dependent on the range in $^{107}Ag/^{109}Ag$ values for

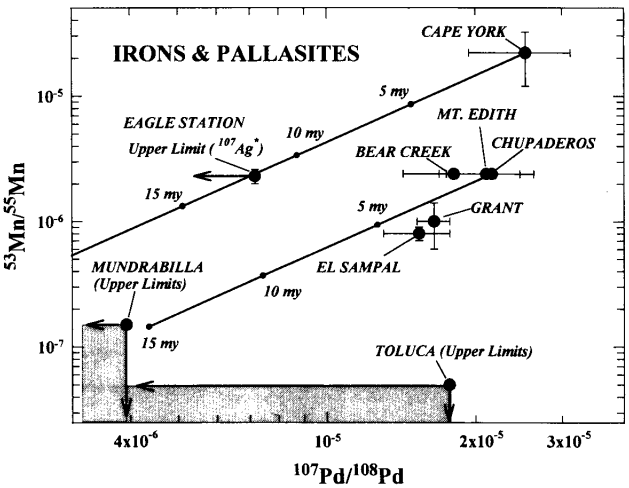

Fig. 11. A coupled $^{53}Cr^*/^{53}Mn$ and $^{107}Pd/^{108}Pd$ diagram (log scales) showing data from a few meteorites. The data on Mundrabilla, Toluca and Eagle Station are only upper limits, as shown with arrows. Lines through Cape York and Chupaderos indicate the locus of closed system decays for both ^{107}Pd and ^{53}Mn with an initial value of Cape York and Chupaderos.

normal and it is possible that there is, in fact, no $^{107}Ag^*$ present. Refinement of this bound would be quite difficult unless there are samples with much higher Pd/Ag. We conclude that an intensive comparative study of ^{107}Pd-^{107}Ag and ^{53}Mn-^{53}Cr isotopic systems on more meteorites, with particular emphasis on internal isochrons with associated mineral phases and their petrogenetic evolution are critical to further understanding. This problem is of particular importance since ^{107}Pd and ^{53}Mn are among the few pairs of short-lived chronometers that are found in the same planetary bodies. We note that the possible nucleosynthetic sources of ^{53}Mn are not well identified [cf *Wasserburg and Arnould*, 1987], whereas a plausible ^{107}Pd source appears to be well-defined in some models [*Cameron*, 1993; *Wasserburg et al.*, 1993, 1994].

5. CONCLUSIONS

$^{107}Ag^*$ is found in representatives of iron meteorites from groups IIAB, IIIAB, IVA, IVB, pallasites, mesosiderites and diverse "anomalous" irons. These objects represent different stages in condensation of FeNi metal, aggregation of dust to form planetary bodies, and the differentiation of planetary bodies involving metal melting, metal-sulfide segregation and core formation. Excellent correlations were found between $^{107}Ag/^{109}Ag$ and $^{108}Pd/^{109}Ag$ using metal and troilite from selected individual meteorites and from diverse metal samples from the Gibeon meteorite. These observations clearly demonstrate that $^{107}Ag^*$ is correlated with Pd and is due to the decay of ^{107}Pd ($\bar{\tau}_{107} = 9.4 \times 10^6$ y) in planetary bodies of the solar system. Using the inferred $^{107}Pd/^{108}Pd$ of 2.5×10^{-5} for Gibeon (IVA) as a reference, we calculate model ages (ΔT) for all the metal samples exhibiting $^{107}Ag^*$. It is found that almost all data lie within a narrow time band of 12 my, independently of meteorite class. The IVB meteorites give model ages typically 3.5 to 6.5 my younger than the IVA meteorites. The meteorites, Tlacotepec and N'Goureyma, are much younger and are an exception to the rule of a narrow time band.

There are some samples (e. g., group IVA) which have troilites with $^{107}Ag^*$ that is far in excess of that produced by *in situ* decay. In other cases (e. g. some group IVB and AN), this radiogenic Ag in FeS could be readily produced by re-equilibration or re-melting in a high Pd/Ag environment typical of iron meteorites.

It is shown that the diverse meteorites studied exhibit a relatively narrow range in Pd/Ni roughly equal to $(Pd/Ni)_\odot$. Each meteorite class appears to form groups of well-defined elongated clusters on a Pd vs Ni graph that transect the solar ratio. In contrast, the data on a ^{109}Ag vs Ni graph exhibit a very wide range in $^{109}Ag/Ni$ as compared to the solar value. The range is from ~4 x 10^{-2} x $(^{109}Ag/Ni)_\odot$ for group I to extreme Ag-depletions of 1.2 x 10^{-5} to 1.2 x 10^{-4} x $(^{109}Ag/Ni)_\odot$ for the IVA, IVB meteorites. This reflects a wide range in so called "volatile" content as inferred by other workers based on elements such as Ga, Ge, Au, Cu, Sb and P.

The ^{107}Pd-^{107}Ag chronometer reflects the time of major chemical fractionation of Pd and Ag. The scenarios we have inferred include two basically different fractionation processes, namely nebular and planetary.

For the very volatile-depleted FeNi-rich meteorites (VDM), the possible processes are:

(1) Formation of FeNi metal condensates (containing PGE with the somewhat later condensing Pd) leaving Ag behind in the gas phase.

(2) Segregation of this FeNi metal and many silicates as solids at elevated temperatures (~900° K).

(3) Segregation of the later condensates of volatile and moderately volatile elements (including Ag) from the earlier condensed FeNi metal and associated silicates.

(4) Reaction of FeNi metal with H_2S (gas) to form Ag-free FeS.

(5) Aggregation into planetary bodies with subsequent melting with some FeNi-FeS separation.

For the case of FeNi-rich meteorites not depleted in volatiles, the possible processes are:

(1) Aggregation of average solar system condensates and reaction products with FeS formed by reaction of H_2S (gas) with dispersed material.

(2) Planetary body formation.

(3) Melting with FeNi-FeS separation to produce metal with high PGE content and $^{108}Pd/^{109}Ag$ ~ 50 - 100.

The spectrum of intermediate Pd/Ag ratios in many meteorites is considered to be a blend of the above extreme

scenarios. Some of the mechanisms outlined above are in accord with the views of others workers [e. g., *Scott*, 1972; *Kelly and Larimer*, 1977; *Larimer*, 1988]. Many of the specific details are not clear to us, but we feel that both nebular and planetary differentiation processes are required to explain the observations. It is not evident that condensation from a mix of solar composition is required. Possibly condensation from matter from which H_2 has been essentially removed may be involved. This might be the result of reheating and evaporation of planetary material due to planetary collisional processes after major gas loss from the nebula had already taken place. The fractionation and condensation sequence to be expected from a nearly H-free system but containing S may provide an alternative possibility.

In considering the role of alternative mechanisms, we have focussed on nebular condensation and on Ag fractionation between FeS and FeNi in liquid-liquid or liquid-solid in planetary processes. None of the data indicate that the K_{Ag} is sufficiently large as to yield the observed major fractionations in several meteorite classes. (Assuming $K_{Ag} \approx 20$, FeS removal could account for shifts in the Ag content of FeNi by a factor of only 10 to 50.) We note that FeNi condenses out at high temperatures while FeS is formed by a gas reaction of H_2S at low temperatures with the earlier formed Fe metal. In our model, it is assumed that this FeNi metal is segregated from those phases containing Ag that condensed at intermediate temperatures. Following these arguments, it is concluded that those metals highly to extremely depleted in ^{109}Ag are a result of fractionation and separation at elevated temperatures of FeNi during local heating and subsequent cooling of parts of the solar nebula. These objects later reacted with H_2S to form some FeS. Subsequently during planetary melting, some redistribution and removal of $^{107}Ag^*$ took place by sulfide extraction (e. g., IVB meteorites). The IVA meteorites did not undergo this later processing. In contrast, the Group I meteorites reflect FeS separation in an environment where Ag and other volatiles were present in planetary bodies in nearly solar abundances. The Pd-Ag chronometer, therefore, is taken to reflect a combination of nebular condensation and planetary differentiation processes, but where the fractionation processes most effectively separating Pd from Ag are a nebular condensation stage. The detailed behavior of Ag in the condensation and segregation processes with particular connection to the formation and segregation of carrier phases (possibly Cu metal) remains to be addressed. The "chalcophile" behavior of Ag is considered to be appropriate only in regimes or in planetary processes in the presence of FeS which only forms at low nebular temperatures along with minor phases that may contain substantal Ag.

Evidence of both ^{107}Pd and ^{53}Mn exists in some meteorites. However, there is a wide spread in the inferred $^{53}Mn/^{55}Mn$ compared to that of $^{107}Pd/^{108}Pd$ and these results are in conflict. We conclude that redistribution of ^{53}Cr in the extended cooling history of these meteorites may be responsible for $^{53}Cr^*$ redistribution by diffusion or by late growth of the related microscopic phases with high Mn/Cr (e.g., phosphate, olivine and alabandite).

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REFERENCES

Birck, J. L., and C. J. Allègre, Manganese-chromium isotope systematics and the development of the early solar system, *Nature, 331,* 579-584, 1988.

Buchwald, V. F., *Handbook of Iron Meteorites*, Univ. California Press, 1418 pp., Berkeley, 1975.

Burbidge, E. M., G. R. Burbidge, W. A. Fowler and F. Hoyle, Synthesis of the elements in stars. *Rev. Mod. Phys., 29,* 547-650, 1957.

Cameron, A. G. W., Nucleosynthesis and star formation. In *Protostars and Planets III*, eds. E. H. Levy and J. I. Lunine (Tucson: Univ. Arizona Press), 47-73, 1993.

Chakraburtty, A. K., C. M. Stevens, H. C. Rushing, and E. Anders, Isotopic composition of Ag in iron meteorites. *J. Geophys. Res., 69,* 505-520, 1964.

Chen, J. H., and G. J. Wasserburg, The isotopic composition of silver and lead in two iron meteorites: Cape York and Grant. *Geochim. Cosmochim. Acta, 47,* 1725-1737, 1983.

Chen, J. H., and G. J. Wasserburg, The isotopic composition of Ag in meteorites and the presence of ^{107}Pd in protoplanets. *Geochim. Cosmochim. Acta, 54,* 1729-1743, 1990a.

Chen, J. H., and G. J. Wasserburg, The presence of ^{107}Pd in the early solar system. *Lunar Planet. Sci. Conf. XXI,* 184-185, 1990b.

Chen, J. H., and G. J. Wasserburg, The Pd-Ag systematics in chondrites and mesosiderites. *Lunar Planet Sci. Conf. XXII,* 199-200, 1991.

Chen, J. H., and G. J. Wasserburg, A comparison between ^{107}Pd and ^{53}Mn chronometers in some meteorites. *Lunar Planet Sci. Conf. XXVI,* in press, 1995.

Davis, A. M., and E. J. Olsen, Phosphates in the El Sampal IIIA iron meteorite have excess ^{53}Cr. *Lunar Planet. Sci. Conf. XXI,* 258-259, 1990.

Dews, J. R., and R. S. Newbury, The isotopic composition of Ag in the Canyon Diablo meteorite. *J. Geophys. Res., 71,* 3069-3081, 1966.

Floran, R. J., Silicate petrography, classification, and the origin of the mesosiderites: Review and new observations. *Proc. Lunar Planet. Sci. Conf. 9th,* 1053-1081, 1978.

Graham, A. L., A. W. R. Bevan, and R. Hutchison, *Catalogue of meteorites*, Tucson: Univ. of Arizona Press, 1985.

Grossman, L., and J. W. Larimer, Early chemical history of the solar system. *Rev. Geophys. Space Phys., 12*, 71-101, 1974.

Herpfer, M. A., J. W. Larimer, and J. I. Goldstein, A comparison of metallographic cooling rate methods used in meteorites. *Geochim. Cosmochim. Acta, 58*, 1353-1365, 1994.

Hess, D. C., R. R. Marshall, and H. C. Urey, Surface ionization of silver: silver in meteorites. *Science, 126*, 1291-1293, 1957.

Hutcheon, I. D., and E. J. Olsen, Cr isotopic composition of differentiated meteorites: A search for ^{53}Mn. *Lunar Planet Sci. Conf. XXII*, 605-606, 1991.

Jones, J. H., T. M. Benjamin, C. M. Maggiore, C. J. Duffy, and S. R. Hart, Experimental partitioning of Ag, Mo, Pb and Pd between iron metal and troilite. *Lunar Planet. Sci. Conf. XVII*, 400-401, 1986.

Jones, J. H., and M. J. Drake, Experimental investigations of trace element fractionation in iron meteorites, II: The influence of sulfur. *Geochim. Cosmochim. Acta, 47*, 1199-1209, 1983.

Jones, J. H., and D. J. Malvin, A nonmetal interaction model for the segregation of trace metals during solidification of Fe-Ni-S, Fe-Ni-P, and Fe-Ni-S-P alloys, *Metallurgical Transations B, 21B*, 697-706, 1990.

Jones, J. H., S. R. Hart, and T. M. Benjamin, Experimental partitioning studies near the Fe-FeS eutectic, with an emphasis on elements important to iron meteorite chronologies (Pb, Ag, Pd, and Tl). *Geochim. Cosmochim. Acta, 57*, 453-460, 1993.

Kaiser, T., W. R. Kelly, and G. J. Wasserburg, Isotopically anomalous Ag in the Santa Clara and Piñon iron meteorites. *Geophys. Res. Lett., 7*, 271-274, 1980a.

Kaiser, T., W. R. Kelly, and G. J. Wasserburg, Hoba and Tlacotepec: Two new meteorites with isotopically anomalous Ag. *Meteoritics 15*, 310-311, 1980b.

Kaiser, T., and G. J. Wasserburg, What is the origin of ^{107}Ag and ^{109}Ag in nickel-rich ataxites? *Lunar Planet Sci. Conf. XII*, 525-527, 1981.

Kaiser, T., and G. J. Wasserburg, The isotopic composition and concentration of Ag in iron meteorites. *Geochim. Cosmochim. Acta, 47*, 43-58, 1983.

Kallemeyn, G. W., W. V. Boynton, J. Willis, and J. T. Wasson, Formation of the Bencubbin polymict meteoritic breccia. *Geochim. Cosmochim. Acta, 42*, 507-515, 1978.

Kelly, W. R., and J. W. Larimer, Chemical fractionations in meteorites VIII. Iron meteorites and the cosmocheical history of the metal phase. *Geochim. Cosmochim. Acta, 41*, 93-111, 1977.

Kelly, W. R., and G. J. Wasserburg, Evidence for the existence of ^{107}Pd in the early solar system. *Geophys. Res. Lett., 5*, 1079-1082, 1978.

Kelly, W. R., F. Tera, and G. J. Wasserburg, Isotopic determination of Ag in picomole quantities by surface ionization mass spectrometry. *Anal. Chem., 50*, 1279-1286, 1978.

Kracher, A., J. Willis, and J. T. Wasson, Chemical classification of iron meteorites. IX. A new group (IIF), revision of IAB and IIICD, and data on 57 additional irons. *Geochim. Cosmochim. Acta, 44*, 773-787, 1980.

Larimer, J. W., and E. Anders, Chemical fractionations in meteorites II. Abundance patterns and their interpretation. *Geochim. Cosmochim. Acta, 31*, 1239-1270, 1967.

Lugmair, G. W., A. Shukolyukov and C. MacIsaac, The abundance of ^{60}Fe in the early solar system. In *Nuclei in the Cosmos*, (edited by M. Busso, R. Gallino and C. M. Raiteri, pp. 568-571, AIP, New York, 1994.

Malvin, D. J., J. H. Jones, and M. J. Drake, Experimental investigations of trace element fractionation in iron meteorites. III. Elemental partitioning in the system Fe-Ni-S-P. *Geochim. Cosmochim. Acta, 50*, 1221-1231, 1986

Malvin, D. J., D. Wang, and J. T. Wasson, Chemical classification of iron meteorites- X. Multielement studies of 43 irons, resolution of group IIIE from IIIAB, and evaluation of Cu as a taxonomic parameter. *Geochim. Cosmochim. Acta, 48*, 785-804, 1984.

Mermelengas, N., J. R. De Later, and K. J. R. Rosman, New data on the abundance of palladium in meteorites. *Geochim. Cosmochim. Acta, 43*, 747-753, 1979.

Murthy, V. R., Isotopic composition of Ag in an iron meteorite. *Phys. Rev. Lett., 5*, 539-541, 1960.

Murthy, V. R., The isotopic composition of Ag in iron meteorites. *Geochim. Cosmochim. Acta, 26*, 481-488, 1962.

Newsom, H. E., and M. J. Drake, The origin of metal clasts in Bencubbin meteoritic breccia. *Geochim. Cosmochim. Acta, 43*, 689-707, 1979.

Powell, B. J., Petrology and chemistry of mesosiderites II. Silicate texture and composition and metalsilicate relationships. *Geochim. Cosmochim. Acta, 35*, 5-34, 1971.

Prinzhofer, A., D. A. Papanastassiou, and G. J. Wasserburg, Samarium-neodymium evolution of meteorites. *Geochim. Cosmochim. Acta, 56*, 797-815, 1992.

Prombo, C. A., and R. N Clayton, A striking nitrogen isotope anomaly in the Bencubbin and Weatherford meteorites, *Science, 230*, 935-937, 1985.

Rasmussen, K. L., D. J. Malvin , V. F. Buchwald, and J. T. Wasson, Compositional trends and cooling rates of group IVB iron meteorites. *Geochim. Cosmochim. Acta, 48*, 805-813, 1984 .

Saikumar, V., and J. I. Goldstein, An evaluation of the methods to determine the cooling rates of iron meteorites. *Geochim. Cosmochim. Acta, 52*, 715-726, 1988.

Schaudy, R., J. T. Wasson, and V. F. Buchwald, The chemical classification of iron meteorites. VI. A reinvestigation of irons with Ge concentrations lower than 1 ppm. *Icarus, 17*, 174-192, 1972.

Scott, E. R. D., Chemical fractionation in iron meteorites and its interpretation. *Geochim. Cosmochim. Acta, 36*, 1205-1236, 1972.

Scott, E. R. D., J. T. Wasson, and V. F. Buchwald, The chemical classification of iron meteorites-VII. A reinvestigation of irons with Ge concentrations lower than 1 ppm. *Geochim. Cosmochim. Acta, 37*, 1957-1983, 1973.

Scott, E. R. D., and J. T. Wasson, Classification and properties of iron meteorites. *Rev. Geophys. Space Phys., 13*, 527-543, 1975.

Shukolyukov, A., and G. W. Lugmair, Live iron-60 in the early solar system. *Science, 259*, 1138-1142, 1993b.

Stewart, B., D. A. Papanastassiou, and G. J. Wasserburg, Sm-Nd and

RbSr chronology and petrogenesis of mesosiderites. *Geochim. Cosmochim. Acta, 58*, 3487-3509, 1994.

Teshima, J., A. El Goresy, G. J. Wasserburg, and J. H.Chen, A comparative petrologic study of iron meteorites with $^{107}Ag^{*}$ anomalies. *Geochim. Cosmochim. Acta, 50,* 2073-2087, 1986.

Wai, C. M., and Wasson J. T. Nebular condensation of moderately volatile elements and their abundances in ordinary chondrites. *Earth Planet. Sci. Lett., 36*, 1-13, 1977.

Wasserburg, G. J., and M. Arnould, A possible relationship betweenextinct ^{26}Al and ^{53}Mn in meteorites and early solar activity. In *Nuclear Astrophysics*, eds. W. Hillebrandt, R. Kuhfuss, E. Müller, J. W. Truran, (Berlin:Springer Verlag), 262-276, 1987.

Wasserburg, G. J., R. Gallino, M. Busso, and C. M. Raiteri, AGB stars as a source of short-lived radioactive nuclei in the solar nebula. *Lunar Planet. Sci. Conf. XXIV*, 1487-1488, 1993.

Wasserburg, G. J., R. Gallino, M. Busso, and C. M. Raiteri, Asymptotic Giant Branch stars as a source of shortlived radioactive nuclei in the solar nebula. *Astrophys. J., 424*, 412-428, 1994.

Wasserburg, G. J., R. Gallino, M. Busso, J. N. Goswami, and C. M. Raiteri, Injection of radioactive ^{41}Ca in the early solar nebula by an AGB star. *Astrophys. J.*, in press, 1995.

Wasserburg, G. J., and R. J. Hayden, Time interval between nucleogenesis and the formation of meteorites. *Nature, 176*, 130-131, 1955.

Wasson, J. T., The chemical classification of iron meteorites I. A study of iron meteorites with low concentrations of gallium and germanium. *Geochim. Cosmochim. Acta, 31*, 1161-1180, 1967.

Wasson, J. T., The chemical classification of iron meteorites-III. Hexahedrites and other irons with germanium concentrations between 80 and 200 ppm. *Geochim. Cosmochim. Acta, 33*, 859- 876, 1969.

Wasson, J. T., The chemical classification of iron meteorites-IV. Irons with Ge concentrations greater than 190 ppm and other meteorites associated with group I. *Icarus, 12*, 407-423, 1970a.

Wasson, J. T., Ni, Ga, Ge and Ir in the metal of iron meteorites with silicate inclusions. *Geochim. Cosmochim. Acta, 34*, 957-964, 1970b.

Wasson, J. T., *Meteorites - Classification and Properties* (Berlin: Springer Verlag), 316 pp, 1974.

Wasson, J. T., *Meteorites* (New York: W. H. Freeman and Co.), 267 pp, 1985.

Wasson, J. T., and C.-L. Chou, Fractionation of moderately volatile elements in ordinary chondrites. *Meteoritics, 9*, 69-84, 1974.

Wasson, J. T., and J. Kimberlin, The chemical classification of iron meteorites. II. Irons and pallasites with germanium concentrations between 8 and 100 ppm. *Geochim. Cosmochim. Acta, 31*, 2065-2093, 1967.

Wasson, J. T., and R. Schaudy, The chemical classification of iron meteorites-V. Groups IIIC and IIID and other irons with germanium concentrations between 1 and 25 ppm. *Icarus, 14*, 59-70, 1971.

Wasson, J. T., R. Schaudy, R. W. Bild, and C.-L. Chou, Mesosiderites I. Composition of their metallic portions and possible relationship to other metal-rich meteorite groups. *Geochim. Cosmochim. Acta, 38*, 135-149, 1974.

J. H. Chen and G. J. Wasserburg, The Lunatic Asylum, Division of Geological and Planetary Sciences, MS170-25, California Institute of Technology, Pasadena, CA 91125